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GUIDELINES FOR DEVELOPMENT OF A QUALITY ASSURANCE PROGRAM. REFERENCE METHOD FOR MEASUREMENT OF PHOTOCHEMICAL OXIDENTS

Franklin Smith, et al

Research Triangle Institute

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GUIDELINES FOR DEVELOPMENT OF A QUALITY ASSURANCE PROGRAM

Reference Method for Measurement of Photochemical Oxidants

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GUIDELINES FOR DEVELOPMENT OF A QUALITY ASSURANCE PROGRAM

Reference Method for Measurement of Photochemical Oxidants

By

Franklin Smith
A. Carl Nelson, Jr.
Research Triangle Institute
Research Triangle Park, North Carolina 27709

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Project Officer

Joseph F. Walling
Quality Assurance and Environmental Monitoring Laboratory
National Environmental Research Center
Research Triangle Park, North Carolina 27711

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PREFACE

Quality control is an integral part of any viable environmental monitoring activity. The primary goals of EPA's quality control program are to improve and document the credibility of environmental measurements. To achieve these goals, quality control is needed in nearly all segments of monitoring activities and should cover personnel, methods selection, equipment, and data handling procedures. The quality control program will consist of four major activities:

- Development and issuance of procedures
- Intra-laboratory quality control
- Inter-laboratory quality control
- Monitoring program evaluation and certification

All these activities are essential to a successful quality control program and will be planned and carried out simultaneously.

Accordingly, this third manual of a series of five has been prepared for the quality control of ambient air measurements. These guidelines for the quality control

of photochemical oxidant measurements in the atmosphere have been produced under the direction of the Quality Control Branch of the Quality Assurance and Environmental Monitoring Laboratory of NERC-RTP. The purpose of this document is to provide uniform guidance to all EPA monitoring activities in the collection, analysis, interpretation, presentation, and validation of quantitative data. In accordance with administrative directives to implement an Agency-wide quality control program, all EPA monitoring activities are requested to use these guidelines to establish intralaboratory quality assurance programs in the conduct of all ambient air measurements for photochemical oxidants. Your comments on the utility of these guidelines, along with documented requests for revisions(s), are welcomed.

All questions concerning the use of this manual and other matters related to quality control of air pollution measurements should be directed to:

Mr. Seymour Hochheiser, Chief
Quality Control Branch
Quality Assurance and Environmental
Monitoring Laboratory
National Environmental Research Center
Research Triangle Park, North Carolina 27711

Information on the quality control of other environmental media and categorical measurements can be obtained by contacting the following person(s):

Water

Mr. Dwight Ballinger, Director
Analytical Quality Control Laboratory
National Environmental Research Center
Cincinnati, Ohio 45268

Pesticides

Dr. Henry Enos, Chief
Chemistry Branch
Primate and Pesticide Effects Laboratory
Environmental Protection Agency
Perrine, Florida 33157

Radiation

Mr. Arthur Jarvis, Chief
Office of Quality Assurance-Radiation
National Environmental Research Center
Las Vegas, Nevada 89114

During the months ahead, a series of manuals will be issued which describe guidelines to be followed during the course of sampling, analysis, and data handling. The use of these prescribed guidelines will provide a uniform approach in the various monitoring programs which allows the evaluation of the validity of data produced. The implementation of a total and meaningful quality control program cannot succeed without the full support of all monitoring programs. Your cooperation is appreciated.

ABSTRACT

Guidelines for the quality control of Federal reference method for photochemical oxidants are presented. These include:

1. Good operating practices
2. Directions on how to assess data and qualify data
3. Directions on how to identify trouble and improve data quality
4. Directions to permit design of auditing activities
5. Procedures which can be used to select action options and relate them to costs

The document is not a research report. It is designed for use by operating personnel.

This work was submitted in partial fulfillment of Contract Durham 68-02-0598 by Research Triangle Institute under the sponsorship of the Environmental Protection Agency. Work was completed as of June 1973.

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INTRODUCTION

This document presents guidelines for implementing a quality assurance program for the continuous measurement of photochemical oxidants, corrected for interferences due to nitrogen oxides and sulfur dioxide, in the atmosphere using the chemiluminescent reaction between ozone and ethylene.

The objectives of this quality assurance program for the chemiluminescent method of measuring atmospheric photochemical oxidants are to:

(1) provide routine indications for operating purposes of unsatisfactory performance of personnel and/or equipment,

(2) provide for prompt detection and correction of conditions which contribute to the collection of poor quality data, and

(3) collect and supply information necessary to describe the quality of the data.

To accomplish the above objectives, a quality assurance program must contain the following components:

(1) routine training and/or evaluation of operators,

(2) routine monitoring of the variables and/or parameters which may have a significant effect on data quality,

(3) development of statements and evidence to qualify data and detect defects, and

(4) action strategies to increase the level of precision in the reported data and/or to detect instrument defects or degradation and to correct same.

Implementation of a quality assurance program will result in data that are more uniform in terms of precision and accuracy. It will enable each monitoring network to continuously generate data that approach the highest level of accuracy attainable with the chemiluminescent method.

This document is divided into four sections or chapters. They are:

Section I, Introduction - The introduction lists the overall objectives of a quality assurance program and delineates the program components necessary to accomplish the given objectives.

Section II, Operations Manual - The Operations Manual sets forth recommended operating procedures, instructions for performing control checks designed to give an indication or warning that invalid or poor quality data are being collected, and instructions for performing certain special checks for auditing purposes.

Section III, Supervision Manual - The Supervision Manual contains directions for 1) assessing chemiluminescent data, 2) collecting information to detect and/or identify trouble, 3) applying quality control procedures to improve data quality, and 4) varying the auditing or checking level to achieve a desired level of confidence in the validity of the outgoing data. Also, monitoring strategies and costs as discussed in Section IV are summarized in this manual.

Section IV, Management Manual - The Management Manual presents procedures designed to assist the manager in 1) detecting when data quality is inadequate, 2) assessing overall data quality, 3) determining the extent of independent auditing to be performed, 4) relating costs of data quality assurance procedures to a measure of data quality, and 5) selecting from the options available the alternative(s) which will enable one to meet the data quality goals by the most cost-effective means. Also, discussions on data presentation and personnel requirements are included in this manual.

The scope of this document has been purposely limited to that of a field document. Additional background information is contained in the final report under this contract.

OPERATIONS MANUAL

GENERAL

This operations manual sets forth recommended operating procedures for the continuous measurement of ozone in the atmosphere using gas-phase chemiluminescence. Quality control procedures and checks designed to give an indication or warning that invalid or poor quality data are being collected are written as part of the operating procedures and are to be performed by the operator on a routine basis. In addition, the performance of special quality control procedures and/or checks as prescribed by the supervisor may be required of the operator on certain occasions.

The accuracy and/or validity of data obtained from this method depends upon instrument performance and the proficiency with which the operator performs his various tasks. Deviations from the recommended operating procedures may result in the collection of invalid data or at least reduce the quality of the data. The operator should make himself familiar with the manufacturer's operational instructions and with the rules and regulations concerning the Reference Method as written in the Federal Register, Vol. 36, No. 84, Part II, April 30, 1971 (reproduced as the Appendix of this document).

For illustration purposes, directions throughout this document are written in terms of a 24-hour sampling period (i.e., 24 hours between zero and span calibrations), and an auditing or checking level of 7 checks out of a lot size of 100 sampling periods. Sampling period durations and auditing levels are subject to change by the supervisor and/or manage-. Such change would not alter the basic directions for performing the operation. Also, certain control limits as given in this manual represent best estimates for use in the beginning of a quality assurance program and are, therefore, subject to change as field data are collected.

It is assumed that an analyzer meeting the reference method specifications has been set up and checked out according to the manufacturer's directions by an experienced technician.

OPERATING PROCEDURES

The sequence of operations to be performed during each sampling period is given in Figure 1. Each operation or step in the process is identified by a block. Quality checkpoints in the measurement process, for which appropriate quality control limits are assigned, are represented by blocks enclosed by heavy lines. Other checkpoints involve go/no-go checks and/or subjective judgments by the operator with proper guidelines for decision-making spelled out in the procedures. *These operations and checks are discussed sequentially as one progresses step by step through the sequence of actions in Figure 1.*

ANALYZER CALIBRATION

1. CHECK CYLINDER PRESSURE ON ETHYLENE AND COMPRESSED AIR CYLINDERS BEFORE EACH SAMPLING PERIOD. REPLACE AS REQUIRED.

2. PERFORM MULTIPOINT/ZERO AND SPAN CALIBRATIONS AS SCHEDULED OR AS REQUIRED TO MEET PERFORMANCE STANDARDS.

3. RECORD SETTING OF ZERO AND SPAN CONTROL KNOBS AFTER EACH CALIBRATION.

SAMPLING

4. PLACE ANALYZER IN SAMPLING MODE BY SETTING THE FUNCTION SWITCH, RANGE SELECTOR SWITCH, AND THE TIME CONSTANT SELECTOR SWITCH TO SPECIFIED POSITIONS FOR SAMPLING.

5. CHECK AND, IF NECESSARY, ADJUST ETHYLENE PRESSURE AND SAMPLE + ETHYLENE FLOW RATE TO SPECIFIED VALUES FOR SAMPLING.

6. VISUALLY CHECK THE RECORDING SYSTEM FOR PROPER OPERATION. SERVICE AS REQUIRED.

7. A SAMPLING PERIOD IS DEFINED AS MONITORING TIME BETWEEN SUCCESSIVE ZERO AND SPAN CALIBRATIONS. NO ADJUSTMENT OF ANALYZER CONTROLS ARE MADE WHILE MONITORING.

OPERATIONAL CHECKS

8. AFTER EACH SAMPLING PERIOD CHECK AND COMPARE CONTROL SETTINGS WITH SETTINGS FROM STEP 3 ABOVE.

9. READ AND COMPARE ETHYLENE PRESSURE AND SAMPLE + ETHYLENE FLOW RATE WITH VALUES FROM STEP 5 ABOVE.

10. VISUALLY CHECK SAMPLE INTRODUCTION SYSTEM FOR BREAKS, LEAKS, AND PARTICULATE DEPOSITS. CHECK SHELTER TEMPERATURE FOR PROPER OPERATION. CHECK AND REPLACE FILTERS PERIODICALLY.

11. VISUALLY CHECK THE RECORDING SYSTEM FOR PROPER OPERATION OVER THE PAST SAMPLING PERIOD.

12. VISUALLY CHECK THE RECORDED DATA FOR SIGNS OF EQUIPMENT MALFUNCTIONS, EXCESSIVE POLLUTANT LEVELS, OR UNUSUAL DIURNAL PATTERNS.

DATA PROCESSING

13. REMOVE RECORDED DATA FROM THE RECORDER AND EDIT IN PREPARATION FOR DATA REDUCTION.

14. CONVERT STRIP CHART DEFLECTIONS TO O_3 CONCENTRATION IN ppm AS HOURLY AVERAGES.

15. COMPLETE SAROAD FORM FOR HOURLY AVERAGES AND DOCUMENT RESULTS OF ANY SPECIAL CHECKS. FORWARD TO SUPERVISOR.

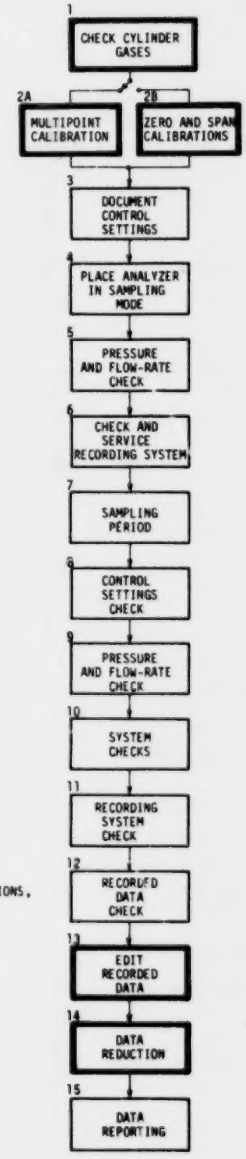


Figure 1: Operational Flow Chart of the Measuring Process

The operator is also responsible for maintaining certain records. Specifically, the following log books are maintained on site:

(1) Operational Data Log Book. Completed daily check sheets (see Figure 7) are filed in the operational data log book. Also, special quality control checks are recorded on the form in Figure 8 and stored in this log book.

(2) Calibration Log Book. Completed calibration conversion sheets, calibration curves, and calibration schedules are filed in the calibration log book.

(3) Maintenance Log Book. Maintenance records and schedules make up the maintenance log book. Schedules should be made up from manufacturer's recommendations and altered as detailed experience suggests.

A typical monitoring setup consisting of a sample introduction system, calibration system, analyzer system, and data recording and display system is illustrated in Figure 2.

Analyzer Calibration

Procedures for performing three types of analyzer calibrations are presented herein. The three types include:

(1) a multipoint absolute or primary calibration,

(2) a multipoint secondary calibration, and

(3) a zero and span check/calibration.

A multipoint absolute or primary calibration is performed with the apparatus assembled as shown in Figure 2. An ozone source or generator is used to generate test atmospheres. The ozone concentration of the generator output is established by analysis, utilizing the neutral buffered potassium iodide (KI) method as the primary standard.

A multipoint secondary calibration is performed using an ozone generator that has been calibrated against a primary standard (i.e., the KI Method) as a secondary standard. The apparatus is connected as shown in Figure 2 with the exception that the KI sampling train is not required.

Zero and span checks or calibrations are made using an internal ozone generator, if the analyzer is so equipped, or an external generator of the type used in primary and secondary calibrations.

When first implementing a quality assurance program, it is recommended that, unless the data are already available, at least five (5) primary calibrations extending over a time interval of at least two weeks be performed. These data should then be used to construct an average calibration curve for the ozone generator as described in the section on Secondary Calibrations on page 14. Also, the data can be used to rank the individual contributions

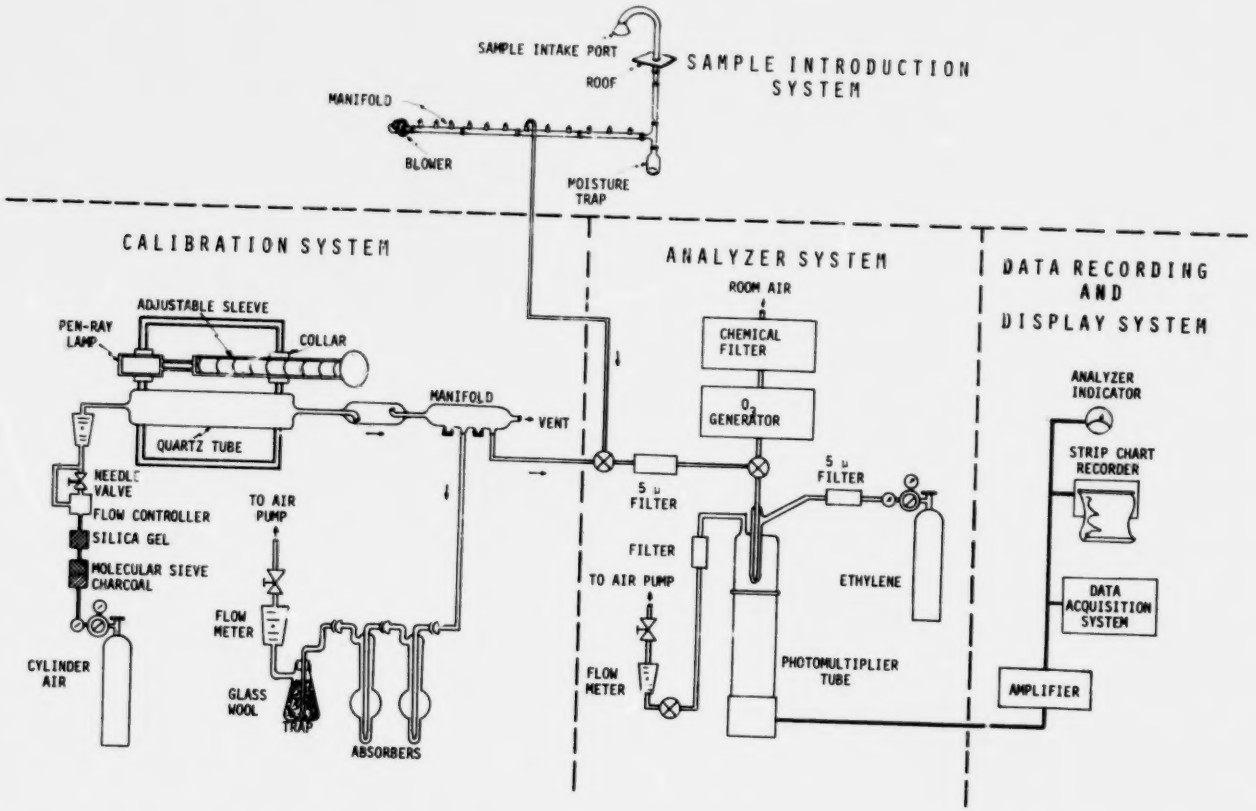


Figure 2: Ozone Monitoring System Flow Chart

of the generator, KI Method, and analyzer to total data variation by plotting three graphs: 1) sleeve setting vs. O_3 by the KI Method, 2) sleeve setting vs. analyzer response, and 3) analyzer response vs. O_3 by the KI Method and comparing the data spread about the best-fit curve for each graph. Once the above data are available, the ozone generator can be used as a secondary standard for calibrating ozone analyzers. The generator is periodically calibrated against the KI Method as discussed on page 14.

Check Cylinder Gases (Step 1)

Check the cylinder pressure on the ethylene and the compressed air cylinders before each sampling period. Under normal operating conditions replace the cylinder of ethylene when its pressure drops below 350 kN/m^2* (50 psi). Replace the compressed air cylinder when its pressure drops below 700 kN/m^2 (100 psi).

Multipoint Calibration (Step 2A)

A multipoint calibration as discussed here refers to a calibration consisting of at least 5 data points corresponding to approximately 0, 10, 20, 40, and 80 percent of full scale. The precision of the KI Method decreases rapidly for concentrations less than about 0.05 ppm.+ Therefore, the first upscale point above zero should be at least 0.05 ppm. For analyzer ranges of less than 0.5 ppm, the calibration points should be evenly distributed between 0.05 ppm and full scale.

Frequency of Calibration - A multipoint calibration, either primary or secondary, is required when:

(1) the analyzer is first purchased,

(2) the analyzer has had maintenance which could affect its response characteristics,

(3) the analyzer has been transferred to a site where the ambient pressure is significantly different from calibration conditions, or

(4) when results from the auditing process show that the desired performance standards are not being met (see page 31).

---

*Throughout this document pressure is converted by the approximate relationship of 1 psi ≈ 7 kN/m^2.

+At 25°C and 760 mmHg conversion from ppm O_3 (Vol/Vol) to µg O_3/m^3 (Mass/Vol) can be made as follows: µg O_3/m^3 = ppm $O_3 \times 1.96 \times 10^3$.

Primary Calibration Procedur s - A primary calibration of an ozone analyzer is performed according to the following procedures:

(1) Obtain or prepare necessary reagents. See Section 6 of the Appendix for reagent specifications and instructions for their preparation.

(2) Prepare a Potassium Iodide (KI) calibration curve as directed in Section 8 of the Appendix. Plot absorbance (y-axis) versus total ozone (x-axis) for the 6 data points on graph paper. Construct a best-fit curve (it should be a straight line up to at least 0.5 ppm) by eye or by using a curve fitting technique such as the method of least squares.

(3) Determine the deviation of each plotted point from the best-fit curve by taking the absorbance value for the plotted point, A_p, and the absorbance value from the best-fit curve, A_c, for the same value of total ozone and compute the difference or deviation, d, by

$$d = A_p - A_c.$$

(4) Rerun any point deviating more than $\pm$ 0.03 absorbance units from the best-fit curve. If the check value also deviates more than $\pm$ 0.03 absorbance units from the curve, redo all the points and construct a new calibration curve.

(5) Repeat the above procedure until an acceptable calibration curve is obtained (i.e., all points are within $\pm$ 0.03 absorbance units of the calibration curve).

(6) Assemble apparatus as shown in Figure 2. See Section 5 of the Appendix for apparatus specifications.

(7) Perform the instrument calibration as directed in Subsection 8.2 of the Appendix.

(8) Fill in the required information on a calibration data sheet as shown in Figure 3.

(9) Run a blank as instructed in Subsection 8.2.2.1 of the Appendix. Adjust the analyzer's zero control knob until the strip chart trace corresponds to the line representing 5 percent of the strip chart width above the chart zero or baseline. This displacement is to allow for possible negative zero drift. If the strip chart already has an elevated baseline, use it as the zero setting.

SAMPLING STATION NAME/NUMBER _____ DATE _____

ANALYZER MODEL _____ SERIAL NUMBER _____

OZONE GENERATOR MODEL _____ SERIAL NUMBER _____

TYPE OF CALIBRATION: PRIMARY [ ] SECONDARY [ ]

OPERATOR _____

ZERO CONTROL SETTING _____ SPAN CONTROL SETTING _____

Calibration Point	Generator Sleeve Setting (mv)	Ozone Concentration By KI (ppm)	Analyzer Response (% chart deflection)
1			
2			
3			
4			
5			
6			

Figure 3: Calibration Data Sheet

(10) Set the generator sleeve to the position giving an ozone concentration output approximately equal to 80 percent of full scale. Caution: the warm-up time necessary for the O_3 generator to stabilize varies from 30 minutes to several hours depending on the generator (Ref. 1). When setting up the equipment, the O_3 generator should be set to give some upscale value and monitored with the analyzer until two successive 10-minute readings show no change other than the normal 1 or 2 percent variation. The system should be allowed 15 minutes to stabilize each time the generator sleeve setting is changed.

Adjust the analyzer's span control knob until the deflection corresponds to the correct percentage of chart as computed by

$$\frac{(\text{ppm } O_3)_s}{(\text{ppm } O_3)_f} \times 100 + 5(\% \text{ zero offset}) = \text{percentage of chart}$$

where $(\text{ppm } O_3)_s$ = average concentration of generator output as measured by the KI Method in ppm,

and $(\text{ppm } O_3)_f$ = full scale reading of the analyzer in ppm.

(11) Lock the zero and span control knobs.

(12) Adjust the generator's sleeve to give ozone concentrations of approximately 40, 20, and 10 percent of full scale in that order.

(13) Record the ozone generator's sleeve setting in mm (various scales are used on the different generators; millimeters are used throughout this text for illustration purposes only), ozone concentration as measured by the KI Method in ppm, and the analyzer response in percent chart deflection (units of current or voltage may be used; all procedures given herein assume that a strip chart recorder is being used) on the calibration data sheet in Figure 3.

(14) Construct a generator calibration curve of sleeve setting (y-axis) versus ozone concentration in ppm (x-axis) as illustrated in Figure 4. Record on the calibration curve the air flow rate, room temperature, and barometric pressure at which the calibration was made. Draw a best-fit straight line for the 5 data points by eye or using a curve-fitting technique such as the method of least squares. Check all points and identify any that deviate more than $\pm$ 12* percent from the best-fit curve. To get the percent deviation for a particular sleeve setting, take the concentration measured by the KI Method, $(\text{ppm } O_3)_m$, and for the same sleeve setting, the concentration read from the best-fit curve, $(\text{ppm } O_3)_t$, and compute:

$$\text{percent deviation} = \frac{(\text{ppm } O_3)_m - (\text{ppm } O_3)_t}{(\text{ppm } O_3)_t} \times 100.$$

(15) Construct an analyzer calibration curve of deflection as percent of strip chart versus ozone concentration in ppm as illustrated in Figure 5. Draw a straight line passing through the zero and span points. Check the three intermediate upscale points. They should fall on or close to the straight line and exhibit a randomness about the line (i.e., all three of the points should not be off in the same direction). Identify any point deviating more than $\pm$ 12 percent from the best-fit curve (see procedure 14 above for computing percent deviation).

(16) Rerun any point identified as deviating more than $\pm$ 12 percent on either one or both of the calibration curves. Average the original and rerun values and replot.

(17) Repeat procedures 14, 15, and 16 until acceptable calibration curves are obtained (i.e., until all points are within $\pm$ 12 percent of the best-fit curve.

(18) Fill in the calibration conversion sheet of Figure 6 from the calibration curve.

---

*This value was derived from an analysis of EPA in-house calibration data and represents the 3σ value. For concentrations less than 0.2 ppm, this value is smaller than the 3σ value for repeatability obtained from a collaborative test (Ref. 2). The above data and analysis are contained in the final report of this contract.

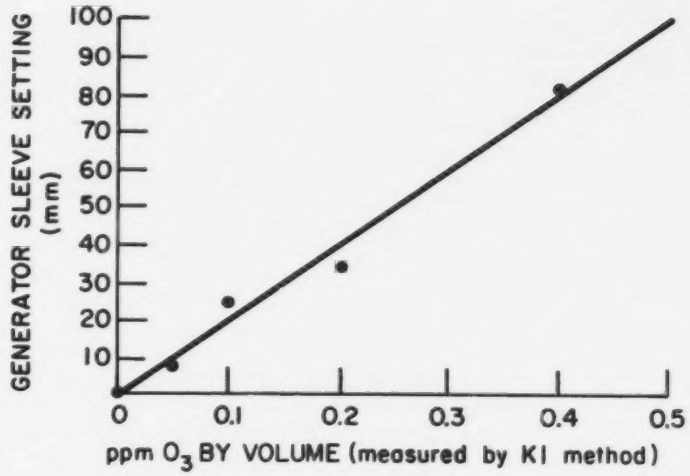


Figure 4: A Sample Ozone Generator Calibration Curve

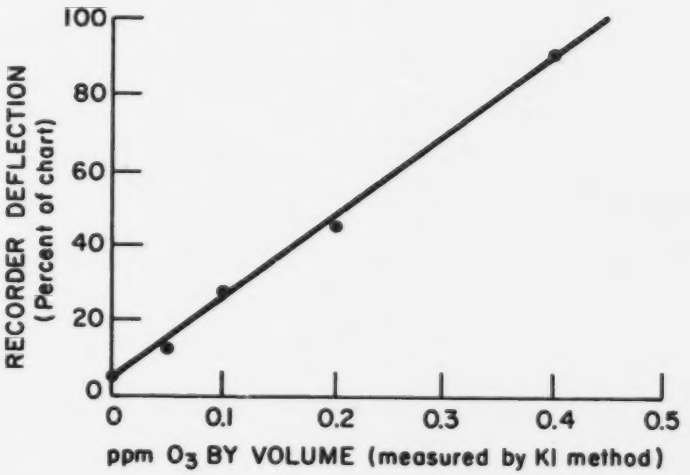


Figure 5: A Sample Ozone Analyzer Calibration Curve

Analyzer No. _____ Date of Calibration_____

% Chart	PPM	% Chart	PPM	% Chart	PPM	% Chart	PPM	% Chart	PPM
0.0		20.5		40.5		60.5		80.5	
0.5		21.0		41.0		61.0		81.0	
1.0		21.5		41.5		61.5		81.5	
1.5		22.0		42.0		62.0		82.0	
2.0		22.5		42.5		62.5		82.5	
2.5		23.0		43.0		63.0		83.0	
3.0		23.5		43.5		63.5		83.5	
3.5		24.0		44.0		64.0		84.0	
4.0		24.5		44.5		64.5		84.5	
4.5		25.0		45.0		65.0		85.0	
5.0									
5.5		25.5		45.4		65.5		85.5	
6.0		26.0		46.0		66.0		86.0	
6.5		26.5		46.5		66.5		86.5	
7.0		27.0		47.0		67.0		87.0	
7.5		27.5		47.5		67.5		87.5	
8.0		28.0		48.0		68.0		88.0	
8.5		28.5		48.5		68.5		88.5	
9.0		29.0		49.0		69.0		89.0	
9.5		29.5		49.5		69.5		89.5	
10.0		30.0		50.0		70.0		90.0	
10.5		30.5		50.5		70.5		90.5	
11.0		31.0		51.0		71.0		91.0	
11.5		31.5		51.5		71.5		91.5	
12.0		32.0		52.0		72.0		92.0	
12.5		32.5		52.5		72.5		92.5	
13.0		33.0		53.0		73.0		93.0	
13.5		33.5		53.5		73.5		93.5	
14.0		34.0		54.0		74.0		94.0	
14.5		34.5		54.5		74.5		94.5	
15.0		35.0		55.0		75.0		95.0	
15.5		35.5		55.5		75.5		95.5	
16.0		36.0		56.0		76.0		96.0	
16.5		36.5		56.5		76.5		96.5	
17.0		37.0		57.0		77.0		97.0	
17.5		37.5		57.5		77.5		97.5	
18.0		38.0		58.0		78.0		98.0	
18.5		38.5		58.5		78.5		98.5	
19.0		39.0		59.0		79.0		99.0	
19.5		39.5		59.5		79.5		99.5	
20.0		40.0		60.0		80.0		100.0	

Figure 6: Table for Converting Trace Deflection in Percent of Chart to Concentration in ppm.

(19) Forward final calibration curves to the supervisor with a description of any trouble encountered during the calibration.

(20) File the calibration data sheet in the calibration log book.

Secondary Calibration Procedures - A secondary calibration of an analyzer is accomplished with a previously calibrated ozone generator. The apparatus setup is as shown in Figure 2 without the KI sampling train.

To qualify the generator as a secondary standard, at least five (5) primary calibrations should be performed. No more than one calibration should be performed on a given day. The five calibrations should cover a period of at least two weeks. Data from the five calibrations are plotted on a graph as shown in Figure 4, and a best-fit curve constructed using the method of least squares. If all calibrations were made at identical sleeve settings, another suitable method for constructing an average calibration curve is to average the concentration values for each sleeve setting. Plot the averages and construct a best-fit curve as shown in Figure 4.

Additional multipoint calibrations of the O_3 generator against the KI Method will be required any time the generator has maintenance which might affect its output characteristics, or when results from the auditing process show that a control sample cannot be measured within $\pm$ (0.01 + 0.075 ppm O_3*) with an analyzer that has just been properly zeroed and spanned with that generator.

Once the generator has been acceptably calibrated (e.g., the ozone concentrations of all plotted points of at least 5 primary calibrations are within $\pm$ 12 percent of the concentrations read from the best-fit curve, or if the averages from the above paragraph were plotted they should not deviate more than $\pm$ $12/\sqrt{n}$ + = 5.4 percent from the best-fit curve), the following procedure is used to calibrate the analyzer.

(1) Set up the equipment as shown in Figure 2 without the KI sampling train. Set the generator sleeve to the normal value used to span the analyzer. Turn on the generator and analyzer and allow to operate until a stable output as measured by the analyzer is obtained. This warm-up time may vary from 30 minutes to several hours (Ref. 1) depending on the generator being used.

(2) Fill in the required information on a calibration sheet as shown in Figure 3.

---

*ppm O_3 = the O_3 concentration of the control sample.

+n = the number of calibrations, in this case 5.

(3) Set the generator output to zero and let the system stabilize. Adjust the zero control knob until the trace corresponds to the line representing 5 percent of the strip chart width above the chart zero or baseline. This is to allow for possible negative zero drift. If the strip chart already has an elevated baseline, use it as the zero setting.

(4) Adjust the generator sleeve setting to give a concentration equivalent to 80 percent of full scale. Allow the system to stabilize. Adjust the span control knob until the deflection corresponds to the correct percentage of chart as computed by

$$\frac{(\text{ppm } O_3)_s}{(\text{ppm } O_3)_f} \times 100 + 5(\% \text{ zero offset}) = \text{percent of chart}$$

where $(\text{ppm } O_3)_s$ = concentration of ozone read from the generator calibration curve,

and $(\text{ppm } O_3)_f$ = full scale reading of the analyzer in ppm.

(5) Lock the zero and span control knobs. Record both knob settings on the form in Figure 3.

(6) Obtain analyzer responses for generator outputs of 40, 20, and 10 percent of full scale in that order.

(7) Record all generator sleeve settings, corresponding ozone concentrations read from the generator calibration curve, and analyzer responses as strip chart deflections on the calibration data sheet of Figure 3.

(8) Construct a calibration curve of recorder deflection (y-axis) versus ozone concentration (x-axis) by drawing a straight line through the zero and span points.

(9) Check all points and rerun any that deviate more than $\pm$ 14 percent from the straight line. Average the original and rerun values and replot. Repeat the procedure until all points are within $\pm$ 14 percent of the straight line.

(10) Fill in the calibration conversion sheet of Figure 6 from the calibration curve.

(11) Forward calibration curve to the supervisor for his approval with a description of any problems encountered during calibration.

(12) File the calibration data sheet in the calibration log book.

Zero and Span Check/Calibration (Step 2B)

A zero and span check is performed before and after each sampling period. An ozone generator as shown in Figure 2 or an internal ozone generator, if the analyzer is so equipped, can be used to perform the zero and span check.

When using an internal generator to span the analyzer, it is recommended that span adjustments not be made if the analyzer response is within $\pm$ 14 percent of the assumed generator output. A secondary or primary calibration should be performed any time larger drifts occur.

The following procedure is followed when a calibrated external generator (secondary standard) is used to span the analyzer.

(1) Connect the apparatus as in Figure 2 (without the KI sampling train).

(2) Turn on the generator and allow time to warm up. After warm-up mark the strip chart trace as unadjusted zero.

(3) Adjust the generator to zero concentration output. Adjust the zero control knob until the strip chart trace corresponds to the 5 percent of chart line. Mark the trace as adjusted zero.

(4) Report any required zero adjustments larger than 0.01 ppm to the supervisor.

(5) Adjust the generator sleeve to give a concentration equivalent to 80 percent of full scale (or any value specified by the supervisor). Allow the system to stabilize. Mark the strip chart trace as unadjusted span. Adjust the span control knob until the deflection corresponds to the correct percentage of chart (see 4 on page 15). Mark the trace as adjusted span with the ozone concentration in ppm.

(6) Report any required span adjustments larger than 0.01 ppm to the supervisor.

(7) Record the unadjusted zero and span readings in ppm on the Daily Check Sheet of Figure 7.

Document Control Settings (Step 3)

After each calibration record the zero and span control knob settings on the Daily Check Sheet of Figure 7 under "New Control Knob Setting."

Any time the high voltage gain setting has to be changed, the new setting is recorded in the maintenance log book. This adjustment is inside the analyzer and would be adjusted before calibrating the analyzer.

Sampling

Place Analyzer in Sampling Mode (Step 4)

Place the analyzer in the sampling mode by setting the function switch, and the time constant selector switch (if the analyzer is so equipped) to appropriate positions for sampling. Record the analyzer range on the Daily Check Sheet of Figure 7.

Pressure and Flow-Rate Check (Step 5)

Check and, if necessary, adjust the sample flow rate to the value specified for sampling. Record the total flow rate (sample air + ethylene) on the Daily Check Sheet of Figure 7 in the column titled "Initial."

Check and, if necessary, adjust the ethylene pressure to the value specified for sampling. The ethylene flow rate should be checked daily with a calibrated rotameter if the analyzer is not equipped with a pressure gauge. It should be so checked at least once a month for analyzers that have a pressure gauge. Record the ethylene pressure/flow rate on the form of Figure 7.

Recording System Check (Step 6)

Check the strip chart recorder for proper operation including

(1) chart speed control setting,

(2) gain control setting,

(3) ink trace for readability,

(4) signs of excess signal noise, and

(5) recorder's deadband according to manufacturer's directions about once a month.

O_3 ANALYZER DAILY CHECK SHEET

Station Name _____ Location _____

Analyzer Number _____ Ozone Generator Number _____

Date	Operator	Sample + Ethylene Flow Rate (ℓ/min)		Ethylene Pressure or Flow Rate	Analyzer Range	Cylinder Pressure kN/m^2		New Control Knob Setting		Unadjusted Readings	
		Initial	Final		(ppm)	Ethy-lene	Air	Zero	Span	Zero	Span

Figure 7: Sample Daily Check Sheet

Automatic data acquisition systems incorporating magnetic tape recorder or punched paper tape are checked for proper operation according to the manufacturer's instructions.

Sampling Period (Step 7)

The sampling period is defined as the time interval between successive zero and span calibrations (usually 24 hours). Do not change control setting on the analyzer or recording system during the sampling period.

Operational Checks

Zero and Span Control Settings (Step 8)

Compare the zero and span control settings to the values recorded on the check sheet (Figure 7) under "New Control Knob Settings" from Step 3. If the settings before and after the sampling period do not agree, note the difference in the data log book and

(1) perform the normal zero and span calibration. If the zero and/or span drifts are both less than $\pm$ 0.01 ppm, continue in the usual manner (this assumes that the original settings were recorded wrong or that the change in setting was not large),

(2) if either the zero or span drift is greater than $\pm$ 0.01 ppm, mark the data invalid and report the situation to the supervisor. Continue normal operations.

Sample Flow Rate (Step 9)

Read the sample plus ethylene flow rate from the rotameter. Record flow rate (ℓ/min) on Daily Check Sheet (Figure 7) as "Final" value. Compare initial and final readings.

If the change is greater than $\pm$ 10 percent of the initial value, check the ethylene pressure, the particulate filters for plugging, and the sample air pump system for proper operation. Take corrective action. Record the exact magnitude of the change on the form in Figure 8 under "Data Quality Statement" with a description of the corrective action taken and forward to the supervisor.

QUALITY CONTROL CHECKS

City_____ Pollutant_____

Site Location_____ Analyzer Number_____

Site Number_____ Date_____

Supervisor Responsible for Checks (Signature)_____

Auditing Level n checks / N sampling periods	Type of Quality Control Check	Result of Check	Corrective Action Taken	Operator Performing Check

Data Quality Statement:

Figure 8: Sample Form for Reporting Results of Quality Control Checks

Compute percent difference by

$$\frac{Q_i - Q_f}{Q_i} \times 100 = \text{percent}$$

where Q_i = initial flow rate (ℓ/min)

and Q_f = final flow rate (ℓ/min).

System Checks (Step 10)

Temperature control check - Each shelter should be equipped with a temperature-indicating device such as a wall thermometer or a maximum and minimum registering thermometer. Check the thermometer to verify that the temperature control system is operating within limits. Control limits on allowable temperature variations are determined by a supervisor from the temperature variation sensitivity check on page 37 and in conjunction with desired accuracy. If a larger than usual or allowable temperature variation is observed, record the minimum or maximum temperature, cause, and corrective action taken on the form in Figure 8 and forward to the supervisor. If no cause is identified, or if the cause is determined but cannot be corrected immediately, report it verbally to the supervisor before performing a zero and span calibration. Always reset the maximum and minimum registering thermometer after checking temperature variation for a sampling period.

Sample introduction system check - A sample introduction system may consist of an intake port, trap for moisture and large particulates, horizontal sampling manifold, and exhaust blower as illustrated in Figure 2, page 6.

Check the moisture trap for accumulated water and large particles. Remove, clean, and replace the trap if any moisture and/or particulates are present.

Visually check the sample introduction system for breakage, leaks, foreign objects in the intake port (e.g., spider webs, wasp nests), and deposited particulates or excess moisture in the horizontal sampling manifold.

The above checks are made each sampling period (usually daily). Conditions such as a break in the manifold or a leaky joint in the sampling manifold network which could affect data quality are reported with the data by a brief description of the condition under "Data Quality Statements" on the form in Figure 8, page 20, and by marking the strip chart trace as invalid and reporting the situation to the supervisor. Take corrective action and document in maintenance log book.

Particulate filter check - A filter with a porosity of 5 micrometers is used to keep large particles from reaching the sample cell. The primary concern is in replacing the filter before foreign material buildup results in ozone loss. When white teflon filters are used, it is recommended that the filter be checked weekly and replaced at any sign of greying. Experience will suggest how often replacements need to be made for a given site.

Recording System Check and Servicing (Step 11)

Check the recording system for signs of recorder malfunctions that may have occurred during the past sampling period. Specific procedures for checking and servicing will depend on the type of recording system used. Check and service automatic data acquisition systems according to the manufacturer's instructions.

For a strip chart recorder check to see that:

(1) the recorder did not run out of chart paper,

(2) there is a continuous inked narrow trace for the entire sampling period, and

(3) there was a uniform advancement of the chart paper by checking the start and end times on the chart and comparing with actual start and end times.

Malfunctions in the recording system resulting in loss or invalidation of data are corrected and documented in the maintenance log book. The sampling interval affected by the malfunction is identified on the strip chart record for that sampling period.

Service the recorder for the next sampling period:

(1) Check the ink supply and refill if less than 1/4 full.

(2) Install a new roll of chart paper as necessary.

Visual Check of Recorded Data (Step 12)

Check and edit the strip chart record for the past sampling period to detect signs of monitoring system malfunctions and to validate the data.

Typical points to look for which may indicate system problems are:

(1) A straight trace for several hours (other than minimum detectable).

(2) Excess noise as indicated by a wide solid trace or erratic behavior such as spikes that are sharper than is possible with the normal instrument response time.

(3) A long steady increase or decrease in deflection.

(4) A cyclic pattern of the trace with a definite time period indicating a sensitivity to changes in temperature or parameters other than O_3 concentration.

(5) Periods where the trace drops below the zero baseline. This may result from a larger-than-normal drop in the ambient room temperature or power line voltage.

If any of the above conditions are detected, data should be flagged, troubleshooting done, and the supervisor informed. Data should be declared invalid only if malfunction of the instrument is detected; otherwise, the data should be reported.

Also, for data validation, a graph could be prepared by the supervisor from previous data (e.g., 1 year of data) containing the average and $\pm$ 3σ values for the hourly averages for reference when editing data. Figure 9, page 24, is an illustration of such a graph. The occurrence of any one or more of the conditions listed below should be investigated for possible causes (e.g., extra heavy traffic, shift in peak traffic hours, or periods of atmospheric stagnation with high pollution levels):

(1) an estimated 1-hour average falls outside the $\pm$ 3σ limits for that specific hour,

(2) the daily pattern has shifted to left or right by 4 or more hours, and

(3) abnormal pattern such as no peak or two peaks.

Document any causes known or suspected or the absence of any known causes on the form in Figure 8, page 20, under "Data Quality Statement."

Data Processing

Data Handling (Step 13)

At the end of each sampling period, the operator should make certain that the strip chart contains the following information:

(1) Sampling station number and location, pollutant being measured, and operator.

(2) Starting time and date. Ending time and date.

(3) Proper identification of unadjusted zero and adjusted zero traces.

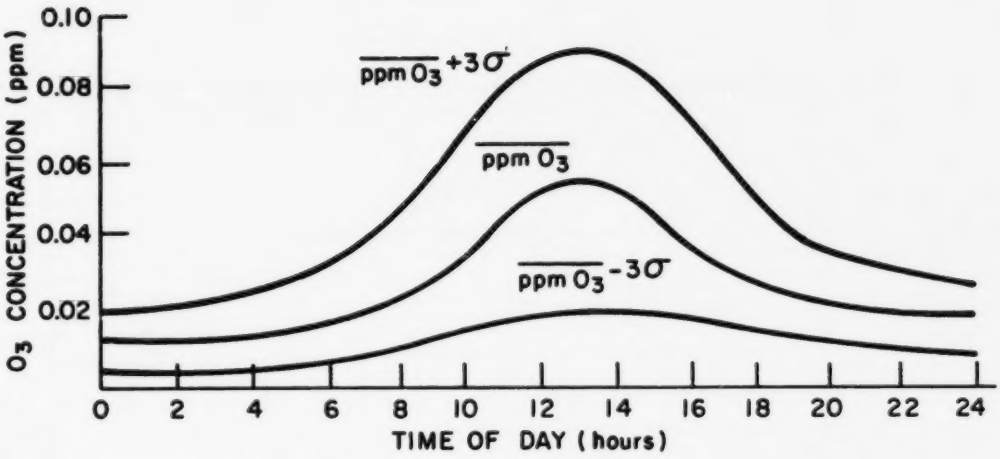


Figure 9: A Sample Graph of the Mean (c) and 3σ Limits of Hourly O_3 Concentrations for a 24-Hour Period

(4) Proper identification of unadjusted and adjusted span traces, and the concentration in ppm of the span gas.

(5) Editing information identifying any periods of invalid data due to equipment failure or other known causes.

Data Reduction (Step 14)

Procedure for reading hourly averages from strip chart recorders - To determine the hourly average concentration from a strip chart record, the following procedures are used:

(1) Obtain the strip chart record for the sampling period in question. The record must have adjusted span and zero traces at the beginning of the sampling period and an unadjusted zero trace at the end of the sampling period.

(2) Fill in the identification data called for at the top of the hourly averages sheet of Figure 10.

CITY_____ SITE NUMBER_____

SITE LOCATION_____ POLLUTANT_____

DATE_____ OPERATOR_____

CHECKER_____

Hour	(1) Reading		(2)ZeroBaseline		(3) Difference		(4) Add +5		(5) PPM	
	Original	Check	Original	Check	Original	Check	Original	Check	Original	Check
0-1										
1-2										
2-3										
3-4										
4-5										
5-6										
6-7										
7-8										
8-9										
9-10										
10-11										
11-12										
12-13										
13-14										
14-15										
15-16										
16-17										
17-18										
18-19										
19-20										
20-21										
21-22										
22-23										
23-24										

Figure 10: Sample Sheet for Recording Hourly Averages

(3) Using a straight edge, draw a straight line from the adjusted zero at the start of the sampling period to the unadjusted zero at the end of the sampling period as illustrated in Figure 11, page 27. This line represents the zero baseline to be used for the sampling period.

(4) Read the zero baseline in percent of chart at the midpoint of each hour interval and record the value on the hourly averages sheet in Figure 10, page 25.

(5) Determine the hourly averages by using a transparent object, such as a peice of clear plastic, with a straight edge at least 1 inch long. Place the straight edge parallel to the horizontal chart division lines. For the interval of interest between two vertical hour lines, adjust the straight edge between the lowest and highest points of the trace in that interval, keeping the straight edge parallel to the chart division lines, until the total area above the straight edge bounded by the trace and the hour lines is estimated to equal the total area below the straight edge bounded by the trace and hour lines. See Figure 11 for an illustrated example.

Read the percentage of chart deflection and record on the hourly average sheet in the column headed Reading under "Original."

Repeat the above procedure for all the hour intervals for which the analyzer was sampling and which have not been marked invalid. Record all values on the hourly averages sheet in the column headed Reading under "Original."

(6) Subtract the zero baseline value (column 2) from the reading value (column 1) and record the difference in column 3.

(7) Add the percent zero offset (column 4) to the difference.

(8) Convert percentage chart values to concentration in ppm using the calibration conversion table (in Figure 6) developed from the calibration curve. Record the ppm values in column 5 on the hourly averages sheet. The "Check" columns will be used in the auditing process and will be discussed in Section II, page 31.

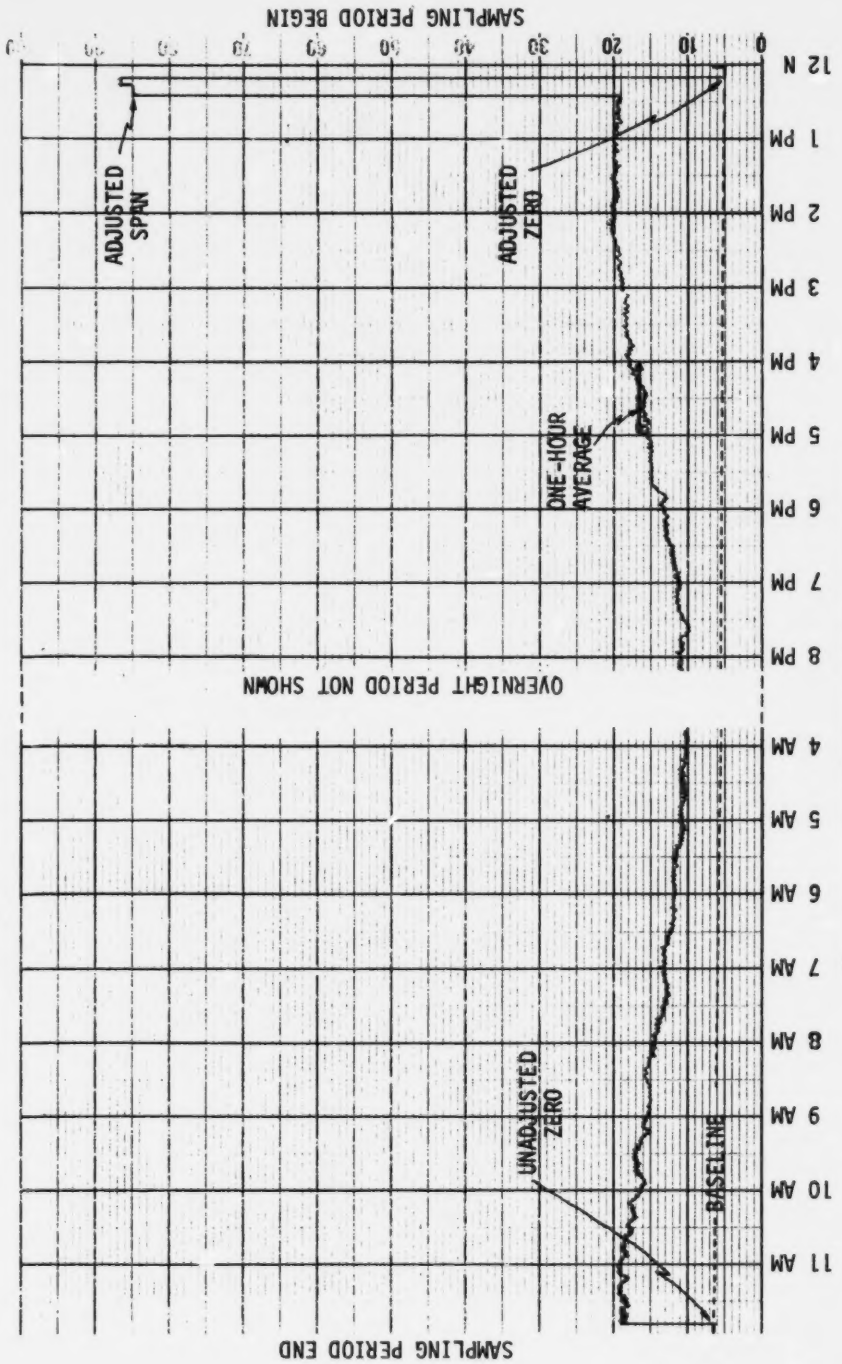


Figure 11: Sample Trace of 24-Hour Sampling Period with Zero and Span Calibrations

Data Reporting (Step 15)

Transcribe information and data from the hourly averages sheet to a SAROAD Hourly Data Form (see Figure 12).

Basic instructions for filling out the SAROAD Hourly Data Form are given below. If the data are to be placed in the National Aerometric Data Bank, further instructions can be obtained from the SAROAD Users Manual APTD-0663.

(1) The SAROAD Hourly Data Form is an approved form for the recording of data observed on averages at intervals of less than 24 hours. In this case the form is to be used for recording hourly averages of ozone observations.

(2) Entries on the upper left of the form (see sample form, Figure 12) provide identification. (Many of these items may already be filled in by the time operators receive the cards.) These are:

(1) Agency - group recording the observations.

(2) City - city in which instrument is operated.

(3) Site - specific location of the sampler within city.

(4) Project name, if any.

(5) Parameter observed - ozone.

(6) Time interval - hourly.

(7) Method - instrumental chemiluminescence.

(8) Units of observation - parts-per-million.

(3) In the upper right hand corner of the SAROAD Hourly Data Form appears three lines of blocks for coding identifying information. These correspond to the card columns of the numbers beneath each box when punched on an 80-column Hollerith card. EPA will assign codes for the first line of blocks to the reporting agency when Site Identification Forms are initially submitted. They consist of a two-digit code for state (SS), a four-digit code for the area of the state in which the sampler is located (CCCC), and a three-digit number specifically identifying the site (XXX). For the remaining two lines of blocks, codes are assigned for each study as follows:

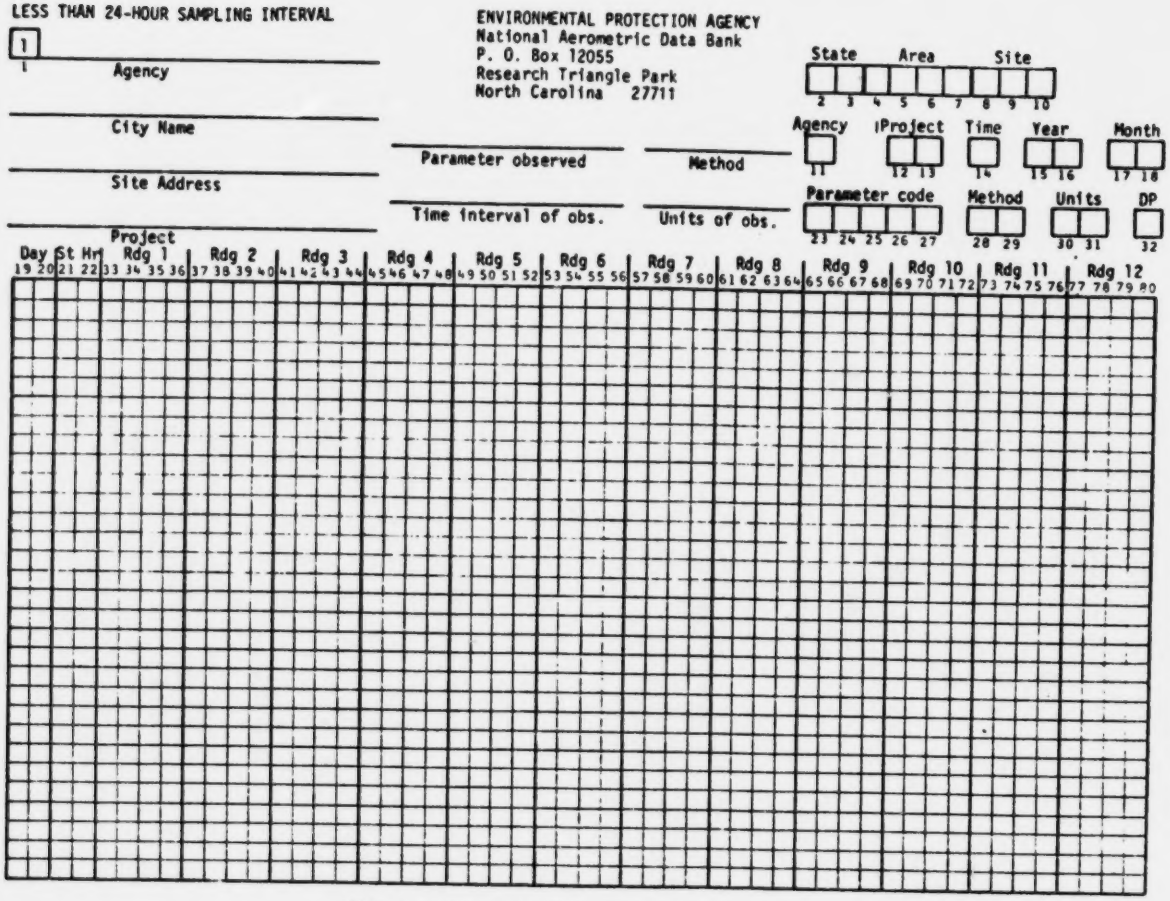


Figure 12: SAROAD Hourly Data Form

(1) Agency - agency code.

(2) Project - project.

(3) Time.

(4) Year.

(5) Month - 01 to 12 for example, as appropriate,

a. July - 07.

b. August - 08.

c. September - 09.

d. October - 10.

e. November - 11.

(6) Parameter code - 44201.

(7) Method - 11.

(8) Units - 07.

(9) DP - 3 (designates the number of places to the right of the decimal point in the value entries).

(4) On the body of the form, the two-block first column, "Day," is the calendar day of the month (e.g., 01, 02). "ST HR" (start hour) calls for either 00 or 12 to denote the starting hour for which data on that line are recorded. Two lines are used for each day's observations. The first line gives "00" (midnight) for "ST HR" and lists the a.m. observations.

(5) Record the hourly averages in the "Rdg" columns: "Rdg 1" would be for either the 0 to 1 hour reading or the 12 to 13 hour reading; "Rdg 2" would be for either the 1 to 2 hour reading or the 13 to 14 hour reading; etc. In entering the hourly averages, the decimal point is located between the first and second column.

For example:

0.01 ppm would be entered as | | 0 | 1 | 0 |

0.1 ppm would be entered as | 0 | 1 | 0 | 0 |.

Report the results of any special quality control checks performed on special form in Figure 8. Attach the special form for quality control checks to the SAROAD form and give to the supervisor.

File the hourly averages sheet in the data log book.

SPECIAL CHECKS FOR AUDITING PURPOSES

In making special checks for auditing purposes, it is important that the check be performed without any special check or adjustment of the system (see Section III, page 51). Two special checks are required to properly assess data quality. A checking or auditing level of 7 checks out of 100 sampling periods is used here for illustration. The supervisor will specify the auditing level to be used according to monitoring requirements Each of the two checks is discussed separately.

Measuring Control Samples

There are two methods for generating control samples that qualify as independent audits. They are 1) a reference ozone generator (i.e., a generator calibrated and maintained independent of generators normally used in the field) and 2) a field ozone generator monitored by the buffered KI Method. See Section III, page 50 for descriptions of the two methods.

A reference ozone generator should be calibrated in the manner described on page 12 under Secondary Calibration Procedures. After the 5 primary calibrations have been performed and an acceptable average calibration curve is constructed, the reference generator should be calibrated against the KI Method at least once a month. Plot all the calibration points on the calibration curve. Continue to use the average calibration curve as long as all plotted points are within $\pm$ 9.5 percent (the assumed 2σ level) of the average curve and continue to show a random scatter. A new average calibration curve should be constructed when single points deviate more than 9.5 percent from the curve or when trends (e.g., all points from a calibration are off in the same directions) are observed such that a new curve using the latest calibration data would deviate more than 5 percent from the average curve.

Reference Generator - When using a reference generator for auditing, it is important that the clean air flow rate is the same as when the O_3 generator was calibrated. Also, room temperature and supply voltage should be as near as possible to calibration conditions. The generator calibration should be verified by the KI Method on site if the site elevation differs by more than 150 m (= 500 ft). The audit procedure is as follows:

(1) Disconnect the field generator output line and connect the line to the output of the reference generator.

(2) Some person other than the regular operator should use the generator calibration curve to set the generator output to be in the range of normally measured ozone concentrations.

(3) Let the control sample flow until the system equilibrates. Have the operator record the analyzer response in ppm.

(4) The person performing or supervising the audit should compare the true value (ppm O_3)$_o$ as read from the generator calibration curve and the measured value as read by the analyzer (ppm O_3)$_m$ by

$$d_1 = \frac{(\text{ppm } O_3)_m - (\text{ppm } O_3)_o}{(\text{ppm } O_3)_o} \times 100 .$$

(5) If d_1 is equal to or greater than $\pm$ 14, reconnect the field generator and have the operator perform a regular zero and span calibration.

(6) Repeat operations 1 through 4.

(7) If the percentage difference, after the zero and span, is still greater than $\pm$ 14, a multipoint primary/secondary calibration is required.

(8) If d_1 is less than $\pm$ 14, continue normal operations.

(9) Record the value of d_1 from 4 above, and (ppm O_3)$_o$ with a short description of trouble, if any, on the form in Figure 8 and forward to the supervisor for his signature.

Buffered KI Method - When using the field generator monitored by the buffered KI Method, proceed in the following manner:

(1) Connect the apparatus as shown in Figure 2.

(2) Position the generator sleeve to give an ozone concentration in the desired range.

(3) A person other than the operator who normally calibrates the analyzer should prepare the KI reagents and determine the generator output using the neutral buffered KI Method.

(4) Record values determined by KI Method and analyzer response in ppm's.

(5) The person performing the audit compares the true concentration $(\text{ppm } O_3)_o$ as measured with KI Method and the concentration as indicated by the analyzer $(\text{ppm } O_3)_m$ in ppm by

$$d_1 = \frac{(\text{ppm } O_3)_m - (\text{ppm } O_3)_o}{(\text{ppm } O_3)_o} \times 100 .$$

(6) If d_1 is less than $\pm$ 15, continue normal operation.

(7) If d_1 is equal to or greater than $\pm$ 15, perform a regular zero and span calibration and remeasure.

(8) If d_1 from the remeasure is still greater than $\pm$ 15, perform a secondary or primary calibration; otherwise, continue normal operation.

(9) Record the value of d_1 (from procedure 6 only) and $(\text{ppm } O_3)_o$ with a short description of trouble, if any, on the form in Figure 8 and forward to the supervisor for his signature.

Data Processing Check

In auditing data processing procedures, it is convenient and allows for corrections to be made immediately if checks are made for each sampling period. Hence, rather than check all 24 hourly averages for 7 days out of every 100 days, it is suggested that 2 one-hour averages be checked each 24-hour sampling period. Also, it is suggested that the 2 highest hourly averages or the 2 hours for which the strip chart trace is most dynamic in terms of spikes be selected for checking by scanning the strip chart record. The check must be independent, that is, performed by an individual other than the one who originanlly reduced the data. The check is made starting with the strip chart record and continuing through the actual transcription of the concentration in ppm on the SAROAD form. This, then, would include reading, calculating, and transcribing or recording errors.

The check is performed in the same manner as that used to process the original data as described in the section on Data Processing, Steps 13 through 15. After all check calculations have been made, the form in Figure 10, page 25, is obtained and the values recorded in the "Check" columns for the appropriate hour. If either one of the two checks differs by as much as $\pm$ 0.01 ppm from the respective original value, all hourly averages for that sampling period should be checked and corrected. In cases where all hourly averages have been checked, the two original, audit checks should be clearly identified on the hourly averages sheet.

SPECIAL CHECKS TO DETECT AND IDENTIFY TROUBLE

The following checks may be required when: 1) a quality assurance program is first initiated in order to determine analyzer/generator performance capabilities and to identify potential problem areas, and 2) at any later time when it becomes increasingly difficult to meet the performance standards of the auditing program to identify and evaluate trouble areas. Procedures for performing a zero drift check, a span drift check, a voltage variation sensitivity check, and a temperature variation sensitivity check are discussed individually.

Zero Drift Check

If available, set up equipment for monitoring and recording on strip chart the analyzer's power source voltage and the ambient room temperature. If such equipment is not available, use a regular A.C. voltmeter capable of measuring between 100 and 130 V.A.C. and connect it across the analyzer power plug. Locate a thermometer or other temperature-indicating device near the analyzer to give a representative reading of the ambient room temperature. A maximum-minimum thermometer is preferred.

(1) With the ozone generator turned off, adjust the air flow through the generator to that normally used during calibration and adjust the strip chart trace to 5 percent of chart.

(2) Start temperature and voltage recorders or read and record the temperature and voltage each hour for the duration of the test.

(3) Let the analyzer operate unadjusted for 24 hours with the zero gas.

(4) From the strip chart(s) and recorded data determine the following:

    (a) difference between lowest (may be negative) and highest values of the zero trace in ppm as ΔC,

    (b) difference between lowest and highest temperatures in °C as ΔT,

    (c) difference between lowest and highest line voltages recorded during sampling period in volts as ΔV,

(5) Document the values of ΔC_o, ΔT_o and ΔV_o in Table 1, page 39, under zero drift check.

(6) Compare the fluctuation of the zero trace with the temperature and voltage fluctuations for similarities (i.e., see if the peaks occur at about the same time). If it appears that the zero trace is sensitive to voltage or temperature changes, individual voltage and temperature sensitivity checks should be made.

Span Drift Check

For this check use an ozone generator that has been checked and shown to maintain a constant output within ± 2 percent for source voltage variations of ± 10 percent (see the Voltage Variation Sensitivity Check on page 36) or place a constant voltage regulator on the generator power source. Set up the equipment as in the Zero Drift Check.

(1) Set the generator output to a value equivalent to at least 50 percent of full scale for the analyzer range normally used for sampling.

(2) Start the temperature and voltage recorders or read and record the temperature and voltage each hour for the duration of the test.

(3) Let the system operate unadjusted for 24 hours.

(4) Read and record the generator flow rate and the ethylene plus sample air flow rate each hour for the duration of the test.

(5) From the strip chart(s) and recorded data determine the following:

(a) difference between the lowest and highest concentration values recorded during the 24-hour test in ppm as ΔC_s,

(b) difference between the lowest and the highest temperatures in °C as ΔT_s,

(c) difference between lowest and highest line voltages recorded during the test period in volts as ΔV_s.

(6) Document the values of ΔC_s, ΔT_s, and ΔV_s in Table 1, page 39, under Span Check.

(7) Compare the fluctuations of the span trace with temperature, voltage, and flow-rate fluctuations for similarities (i.e., see if the peaks occur at about the same time). If it appears that the span trace is sensitive to voltage or temperature changes, individual voltage and temperature sensitivity checks as described below should be performed.

Voltage Variation Sensitivity Check

From the span drift check, if $\Delta C \leq 0.01$ ppm and $\Delta V \geq 10$ volts, do not perform a voltage variation sensitivity check. Report voltage sensitivity as $\Delta C/\Delta V$, where ΔC and ΔV are the actual values observed from the span drift check.

If however, results from the span drift check do not fall in the above category, perform a voltage variation sensitivity test as follows:

(1) Plug the analyzer into a variable voltage transformer (hereafter referred to as a variac) capable of adjusting the power line voltage by $\pm$ 15 volts from the normal line voltage and plug the variac into the regular electrical outlet.

(2) Connect a voltmeter across the variac output leads.

(3) Perform a regular zero and span calibration with the variac adjusted so that the voltmeter reads 115 volts.

(4) With the generator output still set at the span position, adjust the variac until the voltmeter reads 105 volts. Allow the analyzer to stabilize. Identify that portion of the strip chart trace as being at 105 volts.

(5) Adjust the variac until the voltmeter reads 125 volts. Allow the analyzer to stabilize and properly identify the trace.

(6) Read the trace deflection at 105 and 125 volts and convert to concentration in ppm.

(7) Calculate the percent change in concentration per unit change in voltage by

$$\text{percent change/V} = \frac{(\text{ppm } O_3)_{125} - (\text{ppm } O_3)_{105}}{20 \times C_s} \times 100$$

where $(\text{ppm } O_3)_{125}$ = the measured concentration at 125 volts,

$(\text{ppm } O_3)_{105}$ = the measured concentration at 105 volts,

and C_s = O_3 concentration used for the check.

(8) Record the percent change in Table 1 for voltage variation sensitivity.

In addition to the voltage variation sensitivity check for the analyzer, a similar check for the generator should be made about every 6 months.

(1) Connect the generator power plug into a variac capable of adjusting power line voltage by $\pm$ 15 volts from the normal line voltage.

(2) Connect a voltmeter across the variac output leads.

(3) Set the generator output to at least 50 percent full scale for the analyzer range normally used during sampling.

(4) Record generator output as indicated by the analyzer for voltages of 105, 115, and 125.

(5) Calculate the percent change in ozone concentration per unit voltage change by

$$\text{percent change/V} = \frac{(\text{ppm } O_3)_{125} - (\text{ppm } O_3)_{105}}{20 \times C_s} \times 100.$$

(6) If the percent change is equal to or greater than 0.3, a constant voltage regulator should be used to eliminate normal line voltage fluctuations.

(7) If the percent change is less than 0.3, continue normal operations and perform another check in 6 months or when the auditing process shows that performance standards are not being satisfied.

(8) Record the results of the check in the generator maintenance log book.

Temperature Variation Sensitivity Check

From the span drift check, if $\Delta C \leq 0.01$ ppm and $\Delta T \geq 6°C$ (11°F), do not perform a temperature sensitivity check. Report temperature sensitivity as

$$\text{percent change/°C} = \frac{\Delta C}{C_s \times \Delta T} \times 100$$

where ΔC and ΔT are the change in concentration and change in temperature, respectively, as observed from the span drift check,

and C_s is the ozone concentration used during the check.

If however, the above conditions are not satisfied, perform a temperature sensitivity check as follows:

(1) Place the analyzer in a room or chamber where the temperature can be varied by at least $\pm$ 6°C (11°F). The generator should be located outside the room or chamber and maintained at a constant temperature during the check.

(2) Set the generator output to a value equivalent to at least 50 percent of full scale for the analyzer range normally used for sampling.

(3) Let the generator and analyzer warm up sufficiently to get a stable trace.

(4) Set up a temperature-measuring device such as a maximum-minimum thermometer near the analyzer.

(5) Turn the temperature control down 6°C. Allow time for the room temperature and the analyzer trace to stabilize. Read from the thermometer and record on the strip chart the actual temperature.

(6) Turn the temperature control up 12°C from its previous setting (i.e., 6°C above the normal setting). Allow time for room temperature and analyzer to stabilize. Record actual temperature on the strip chart.

(7) Calculate

$$\text{percent change/°C} = \frac{(\text{ppm } O_3)_{T_1} - (\text{ppm } O_3)_{T_2}}{(T_1 - T_2)C_s} \times 100$$

where $(\text{ppm } O_3)_{T_1}$ = concentration in ppm measured at T_1,

$(\text{ppm } O_3)_{T_2}$ = concentration in ppm measured at T_2,

C_s = O_3 concentration used for check,

T_1 = highest temperature (°C),

and T_2 = lowest temperature (°C).

Record the percent change/°C in Table 1 for the temperature sensitivity check.

Treatment of Sensitivity Data

Results from the above checks and estimates (could be actual measurements, if available) of the maximum expected variation of each of the variables under normal operating conditions are recorded in Table 1. Assumes values of expected variation are given for ambient room temperature as $\pm$ 4.5°C from a set value and for voltage as $\pm$ 12 volts from a normal 115 volt source.

The maximum expected error for zero drift is recorded as the value observed from the zero drift check. The results of the span drift check have to be multiplied by the ratio of the maximum ozone concentration measured in the ambient air, $(\text{ppm } O_3)_m$, to the concentration used udring the span drift check, C_s, in order to arrive at a maximum expected error. If any one variable shows a maximum expected error as large as 4 percent of the measured concentration, means of controlling that variable should be considered (see the discussion on Quality Control Procedures in Section III, page 61. For example, if the temperature sensitivity check shows a percentage change of 0.3 and the room in which the analyzer operates has a maximum temperature variation of 9°C, then the maximum possible error in the measured O_3 concentration due to temperature variation would be 2.7 percent (0.3 × 9).

Table 1. ANALYZER EVALUATION DATA

Variable	Result of check	Maximum expected variation	Maximum expected error
Zero drift	ΔC_o =		ΔC_o =
	ΔT_o =		
	ΔV_o =		
Span drift	ΔC_s =		$\Delta C_s \times \frac{(\text{ppm } O_3)_m}{C_s}$ =
	ΔT_s =		
	ΔV_s =		
Temperature	% change/°C =	ΔT = 9°C	(% change) × 9 =
Voltage	% change/V =	ΔV = 24 V	(% change) × 24 =

CALIBRATION OF FLOW-RATE PARAMETERS

Calibrated rotameters are used to measure flow rates in this monitoring system. Three rotameters are used as shown in Figure 2, page 6. Most analyzers have a receptacle for connecting a flow meter to measure the ethylene flow rate. Directions for calibrating the three above mentioned rotameters and for calibrating the flow meter used to measure the ethylene flow rate are given below.

Calibrating Rotameters Against a Wet Test Meter

For the monitoring system as shown in Figure 2, page 6, the rotameters for monitoring the air flow rate through the O_3 generator, the flow rate through the KI sampling train, and the sample air + ethylene flow rate can be calibrated against a wet test meter using air as the calibration gas. Figure 13 shows a typical setup for calibrating rotameters under actual operating conditions. The two boxes labeled system apparatus represent system components used in the monitoring system. As an example, the rotameter in the KI sampling train could be calibrated with the apparatus connected as shown in Figure 14.

Procedure for Calibrating the KI Sampling Train/Sample Air Rotameter - The calibration is performed in the following manner:

(1) Set up the apparatus as shown in Figure 14* making the connections as short as possible and of large enough inside diameter to avoid any appreciable pressure drops.

(2) Start the air flowing through the system and allow to flow for 5 to 10 minutes to allow the water in the wet test meter to reach saturation with the air.

(3) Before and after the complete calibration run, read and record room temperature and barometric pressure. Record average values on the calibration form in Figure 15. Use average values for subsequent calculations.

(4) Adjust the flow rate to about 20 percent of full scale for the rotameter with the needle valve.

(5) Take a pair of timed readings on the wet test meter (for best results use complete revolutions of the wet test meter), under steady flow, for each of five or more uniformly spaced points on the rotameter scale, going from low values to high values. Repeat, going from high to low. Record rotameter reading, total flow, elapsed time of run, manometer reading, and T_m (temperature of the liquid in the wet test meter) for each run on the calibration sheet of Figure 15.

*To calibrate the sample air rotameter connect the outlet side of the wet test meter upstream of the analyzer.

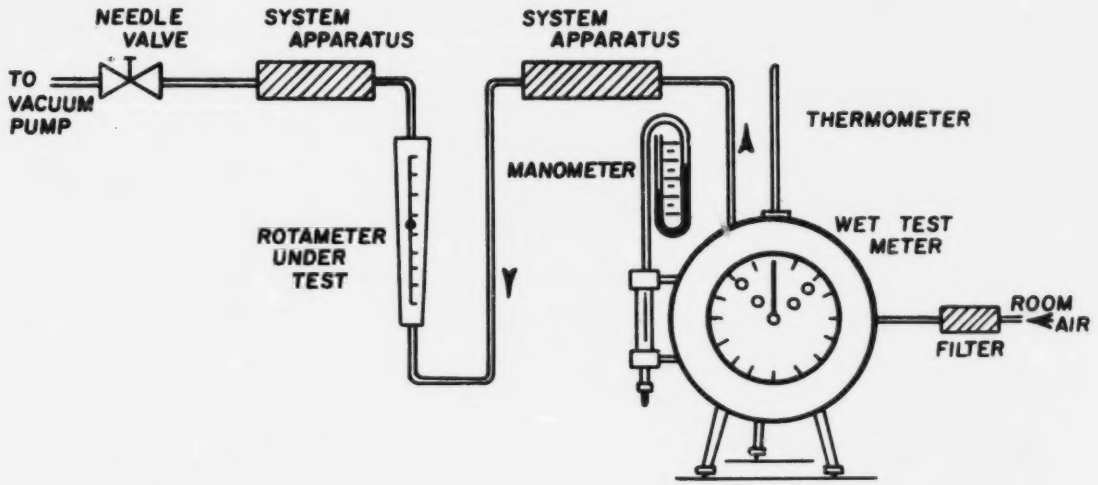


Figure 13: Calibration Assembly Using Wet Test Meter

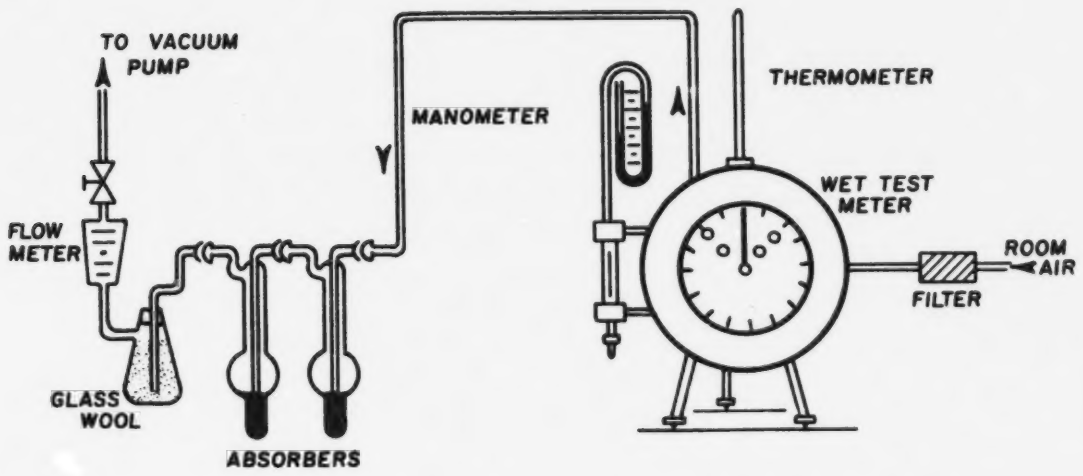


Figure 14: Setup for Calibration KI Sampling Train Rotameter Under Operational Conditions.

Analyzer/Generator _____

Rotameter Serial No. _____

Calibrated With _____

Location _____

Room Temperature (Average) _____ °C

Atmospheric Pressure (Average) _____ mmHg

Calibrated By _____ Date _____

Test Point	Rotameter Reading	Total Flow l	Time min.	Flow rate l/min.	Manometer reading in H_2O	T_m
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						

Figure 15: Rotameter Calibration Data Sheet

(6) Convert all temperature and pressure readings to absolute units.

$$°C + 273 = °K$$

$$\text{in } H_2O \times 1.87 = \text{mmHg}.$$

(7) Calculate indicated flow-rate readings for all recorded rotameter points by dividing the total flow by the elapsed time for that run.

(8) Using the following formula, convert these indicated flow rates to actual flow rates that would be indicated by the rotameter if it were calibrated for air at reference conditions of temperature and pressure.

$$Q_{RC} = Q_m \left(\frac{T_R}{T_m}\right)\left(\frac{P_m}{P_R}\right)$$

where Q_{RC} = flow rate at reference conditions (ℓ/min),

Q_m = flow rate indicated by wet test meter (ℓ/min),

T_R = reference temperature (298°K),

T_m = meter temperature (water temperature for wet test meter, usually same as room temperature) (°K),

P_R = reference pressure (760 mmHg),

and P_m = barometric pressure minus the manometer reading (mmHg). Note: For this setup the manometer reading should be very small (e.g., 0.1 to 0.2 in H_2O).

(9) Prepare a calibration curve of rotameter reading (y-axis) and flow rate at reference conditions (x-axis) by best fit to all points. It should be labeled "corrected for 25°C and 760 mmHg." Figure 16 shows a typical rotameter calibration curve.

Analyzer/Generator_____ Corrected for Air at

Flowmeter No._____ 25°C and 760 mmHg.

Location_____ Calibrated By_____

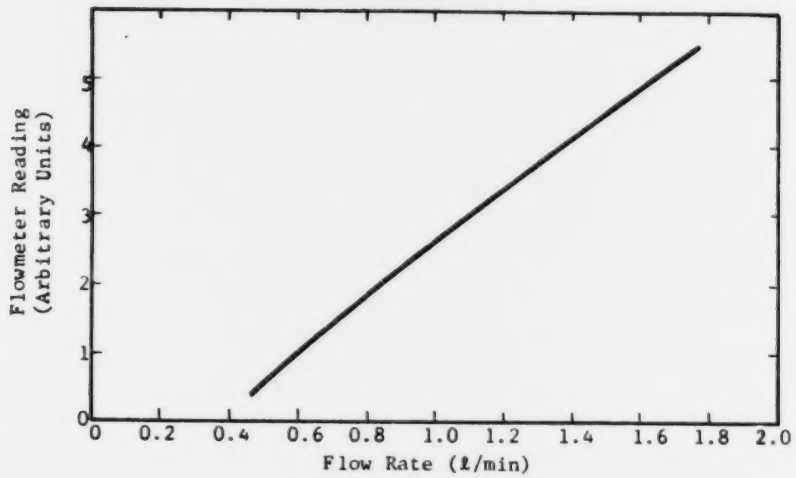


Figure 16: Typical Rotameter Calibration Curve

Procedure for Calibrating the Rotameter in the O_3 Generator Circuit - The calibration is performed in the following manner:

(1) With the monitoring system connected as in Figure 2, page 6, disconnect the KI sampling train and the calibration line to the analyzer from the calibration manifold. Cap all calibration manifold outlets other than the one labeled "vent" in Figure 2.

(2) Connect the vent of the calibration manifold to the inlet side of the wet test meter. Vent the outlet side of the wet test meter to the atmosphere.

(3) Start the air flowing through the system and allow to flow for 5 to 10 minutes to allow the water in the wet test meter to reach saturation with the air.

(4) Before and after the complete calibration run, read and record room temperature and barometric pressure. Record average values on the calibration form in Figure 15. Use average values for subsequent calculations.

(5) Adjust the flow rate to about 20 percent of full scale for the rotameter with the needle valve.

(6) Take a pair of timed readings on the wet test meter (for best results use complete revolutions of the wet test meter), under steady flow, for each of five or more uniformly spaced points on the rotameter scale, going from low values to high values. Repeat, going from high to low. Record rotameter reading, total flow, elapsed time of run, manometer reading, and T_m (temperature of the liquid in the wet test meter) for each run on the calibration sheet of Figure 15.

(7) Convert all temperature and pressure readings to absolute units.

$$°C + 273 = °K$$

$$\text{in } H_2O \times 1.87 = \text{mmHg}.$$

(8) Calculate indicated flow-rate readings for all recorded rotameter points by dividing the total flow by the elapsed time for that run.

(9) Using the following formula, convert these indicated flow rates to actual flow rates that would be indicated by the rotameter if it were calibrated for dry air at reference conditions of temperature and pressure.

$$Q_{RC} = Q_m \left(\frac{T_R}{T_m}\right)\left(\frac{P_m}{P_R}\right)$$

where Q_{RC} = flow rate at reference conditions (ℓ/min),

Q_m = flow rate indicated by wet test meter (ℓ/min),

T_R = reference temperature (298°K),

T_m = meter temperature (water temperature for wet test meter, usually same as room temperature) (°K),

P_R = reference pressure (760 mmHg),

and P_m = barometric pressure plus the manometer reading, minus the vapor pressure of the liquid used in the wet test meter at temperature T_m (mmHg).

(10) Prepare a calibration curve of rotameter reading (y-axis) and flow rate at reference conditions (x-axis) by best fit to all points. It should be labeled "dry air at 25°C and 760 mmHg." Figure 16 shows a typical rotameter calibration curve.

Calibration of the Ethylene Flow-Rate Meter

The ethylene flow rate is approximately 25 cm^3/min. Calibration at this low flow rate requires that a standard other than a wet test meter be used. A soap-bubble meter is recommended. The same configuration as shown in Figure 13 can be used with a soap-bubble meter replacing the wet test meter, provided a moiture trap is located between the bubble meter and system components.

Also, room air or compressed air can be used as the calibration gas. The flow-rate error due to the difference in densities of air and ethylene is about 1 percent. The actual calibration procedure is the same as given in the above subsection with correction to reference conditions being made by the relationship in Step 9, page 45, with the exceptions that T_m becomes the room temperature and P_m is the barometric pressure.

Frequency of Calibrating Rotameters

Rotameter usually require cleaning every six months to a year. It is suggested that they be calibrated after having been cleaned or at any sign of erratic behavior.

FACILITY AND APPARATUS REQUIREMENTS

Facility

A weatherproof shelter or room is required for housing the ozone analyzer. Ideally the shelter or room would be equipped with an automatic, all-seasons air conditioning unit capable of maintaining a pre-set temperature with $\pm$ 3°C (5°F). It is desirable that the heating/cooling be done electrically to guard against the station's emitting pollutants and altering the ambient air quality. A heat pump or a cooling unit with electric resistance heaters would be suitable.

The shelter must be large enough to house the analyzer, any data acquisition equipment, calibration equipment, and storage space for ethylene and dry air cylinders. It should also have adequate working space for the inspection, calibration, and maintenance of the system.

Apparatus

Items of equipment with approximate costs are listed in Table 2. Costs associated with the analyzer, sample introduction system, and ozone generator vary according to the analyzer model and make, size of the sampling station, and type of ozone generator used; hence, only approximate ranges of cost are given for these items.

Each item is checked according to whether it is 1) required in the reference method, 2) used to control a variable or parameter, 3) required for auditing purposes, or 4) used to monitor a variable.

Table 2. APPARATUS USED IN THE CHEMILUMINESCENT METHOD

Item of equipment	Approx cost 1973	Associated error	Reference method	Variable control	Auditing equipment	Variable monitoring
Apparatus						
1. Ozone monitor	5,000		✓			
2. Sample introduction system			✓			
3. Strip chart recorder	1,000			✓		✓
4. Ozone generator	700		✓			
5. Flow controller						
6. Filters and drying columns	50		✓			
7. KI sampling train	75		✓		✓	
8. Spectrophotometer	750		✓			
9. Barometer	50		✓			✓
10. Minimum-maximum thermometer	35	Zero/Span Drift	✓			✓
Reagents						
11. Ethylene (C.P. grade)	50	Sampling/ Calibration				
12. Cylinder air (dry grade)	7	Calibration				
Optional equipment						
13. Ozone generator (for auditing purposes)	700	Meas.Error			✓	
14. Constant voltage regulator	270	Zero/Span Drift		✓		
15. A.C. voltmeter	50	Zero/Span Drift				✓
16. Temperature control (heating/ cooling system)	1,000	Zero/Span Drift		✓		

SUPERVISION MANUAL

GENERAL

Consistent with the realization of the objectives of a quality assurance program as given in Section I, this section provides the supervisor with brief guidelines and directions for:

(1) the collection and analysis of information necessary for the assessment of chemiluminescent data quality,

(2) isolating, evaluating, and monitoring major components of system error,

(3) changing the physical system to achieve a desired level of data quality,

(4) varying the auditing or checking level to achieve a desired level of confidence in the validity of the outgoing data, and

(5) selecting monitoring strategies in terms of data quality and cost for specific monitoring requirements.

This manual provides brief directions that cannot cover all situations. For somewhat more background information on quality assurance see the Management Manual of this document. Additional information pertaining to the chemiluminescent method can be obtained from the final report for this contract or from the literature referenced at the end of Section IV, the Management Manual.

Directions are written in terms of a 24-hour sampling period, an auditing level of n=7 checks out of a lot size of N=100, and an analyzer range of 0 to 0.5 ppm for illustration purposes. Information on different auditing levels is given in the Management Manual.

Specific actions and operations required of the supervisor in implementing and maintaining a quality assurance program as discussed in this section are summarized in the following listing.

(1) Data Assessment

(a) Set up and maintain an auditing schedule.

(b) Qualify audit results (i.e., insure that checks are independent and valid).

(c) Perform necessary calculations and compare to suggested performance standards.

(d) Make corrections or alter operations when standards are exceeded.

(e) Forward acceptable qualified data, with audit results attached, for additional internal review or to user.

(2) Routine Operation

(a) Obtain from the operator immediate reports of suspicious data or malfunctions. Initiate corrective action or, if necessary, specify special checks to determine the trouble; then take corrective action.

(b) On a daily basis, evaluate and dispose of (i.e., accept or reject) data that have been identified as questionable by the operator.

(c) Examine operator's log books periodically for completeness and adherence to operating procedures.

(d) Approve data sheets, calibration data, etc., for filing by operator.

(e) File auditing results.

(3) Evaluation of Operations

(a) Evaluate available alternative monitoring strategies in light of your experience and needs.

(b) Evaluate operator training/instructional needs for your specific operation.

ASSESSMENT OF CHEMILUMINESCENT DATA

Throughout this discussion and the rest of this document, the term "lot" is used to represent a set or collection of objects (e.g., measurements or observations), and the "lot size" designated as N is the number of objects in the lot. The number of objects in the lot to be tested or measured is called the "sample size" and is designated by n. The term "auditing level," used interchangeably with "checking level," is fully described by giving the sample size, n, and the lot size, N.

Required Information

A valid assessment of a batch or lot of chemiluminescent data can be made at a given level of confidence with information derived from two special checks. The two checks are:

(1) measurement of control samples, and

(2) data processing check.

Directions for performing the checks are given in Section II, Special Checks for Auditing Purposes, page 31. Directions for insuring independence and proper randomization in the auditing process and for the analysis of the results are presented in this section.

Collection of Required Information

Measurement of Control Samples - The generation and measurement of control samples and the subsequent treatment of the results are discussed below.

Generation of control samples - Control samples are generated by an ozone generator. A generator used for auditing purposes must either be a reference generator (see page 31) maintained and calibrated by personnel other than the operator(s) maintaining and calibrating the generators regularly used for calibrating the analyzer, or the generator calibrated and maintained by the regular operator can be used and monitored by an individual other than the regular operator using the buffered KI Method. In either case the KI reagents used for calibrating the reference generator or for monitoring the regular generator should be prepared and maintained independent of the reagents used for calibrating the field generators or analyzers.

Procedure for performing check - From the next 100 sampling periods* randomly select 7 periods+ (e.g., one period selected randomly from seven intervals of fourteen sampling periods each would be satisfactory). Then randomly select an hour for each of the 7 periods (it is felt that one hour randomly selected from the 8-hour working day will adequately satisfy the requirements).

---

*One sampling period is defined as one 24-hour day.

+The extent of auditing, i.e., the number of checks, will be discussed in the Management Manual.

At the selected hour within the appropriate sampling period, have the operator set up the equipment and measure a control sample (i.e., set the generator sleeve to some intermediate setting for which the operator would not know the exact concentration output without a calibration curve). Instruct the operator to make no checks or adjustments on the system before making the measurement. The control sample (sleeve setting) can be varied from audit to audit to cover the range of concentrations from about 0.05 to 0.5 ppm. The operator performs the measurement according to the procedures given in Section II, page 31.

Treatment of data - Two values may be obtained from each check. One value represents the measured value of the control sample with no adjustments made to the system prior to measurement. The second value obtained (only if the first value exceeds control limits) is the measure of the control sample obtained after a zero and span calibration has been performed. Results of the second measurement (i.e., the measurement made after a zero and span calibration has been performed) are used to detect and identify trouble and are discussed on page 56. Results of the first measurement are used in assessing data quality and are treated below.

For each measurement or check, compute the difference in the generator output concentration $(\text{ppm } O_3)_o$, and the measured concentration $(\text{ppm } O_3)_m$, in ppm as

$$d_{1j} = (\text{ppm } O_3)_{mj} - (\text{ppm } O_3)_{oj}$$

where j is the j^{th} time that the check has been made during a given auditing period.

Report the value of d_{1j} and $(\text{ppm } O_3)_{oj}$ on the data qualification form of Figure 17.

Data Processing Check - Directions for performing the data processing check and subsequent treatment of the results are discussed below.

Procedure for performing check - Independent checks on data processing errors are made as directed in Section II, page 33. Data processing checks are made each sampling period (24 hours). To insure continuous unbiased checks, it is recommended that the individual performing the checks be changed periodically.

Treatment of data - Two checks are made each sampling period. For each check determine the difference between the check value and the original value. If either check differs by as much as $\pm$ 0.01 ppm from the original value, all hourly averages for that period are checked and corrected. For reporting data quality, the value used for correcting all hour averages (e.g., $\pm$ 0.01 ppm) is reported. In situations where the procedure in

Section IV, page 82 is to be followed for data quality assessment, compute a value for reporting on the form in Figure 17 by

(1) subtracting the check value in ppm from the original value in ppm for each of the two hourly averages that were originally selected for checking,

(2) add the two values computed in (1) above algebraically (i.e., keep track of the signs) and divide by 2, and

(3) report the average in (2) as

$$d_{2j}(\text{ppm})$$

where j is the j^{th} audit performed during the auditing period.

Treatment of Collected Information

Identification of Defects - One procedure for identifying defects is to compare audit results to performance standards. If the standard is exceeded, it counts as one defect. The audit of measuring control samples is the only one used in defining defects. Data processing errors should be corrected when found, and are not, therefore, discussed here.

An audit check in which the value of d_{1j} is greater than $\pm$ (0.01 + 0.075 × ppm O_3) will be considered a defect. The generator output as measured by the KI Method or read from the average calibration curve is used as the value of ppm O_3 for this calculation. This value is assumed to be the 3σ value and is discussed under Suggested Standards for Judging Performance, page 54. As data become available, this limit should be reevaluated and adjusted, if necessary.

Reporting Data Quality - Each lot of data submitted with SAROAD forms or tapes should be accompanied by the minimum data qualifying information as shown in Figure 17. The individual responsible for the quality assurance program should sign and date the form. As an illustration, values from Table 3: Suggested Standards for Judging Performance, page 55, are used to fill in the blanks in Figure 17. The reported auditing rate is the rate in effect at the beginning of the auditing period. An increase or decrease in auditing rate during the auditing period will be reflected by the total number of checks reported. The reason for change should be noted on the form.

Supervisor's Signature_____ Reporting Date _____

Auditing Rate for Data Errors: n = 7, N = 100

Definition of Defect: $|d_{1j}| \geq (0.01 + 0.075 \times \text{ppm } O_3)$

Auditing Rate for Data Processing Errors: n = 2, N = 24

Definition of Defect*: $|d_{2j}| \geq 0.01^{+}$ ppm

Number of Defects Reported_____ (should be circled in the table below)

Audit	Check Values (ppm)				
1. Measurement of (d_{1j}) control samples ($\text{ppm } O_3)_{oj}$	d_{11} $(\text{ppm } O_3)_{01}$	d_{12} $(\text{ppm } O_3)_{02}$	d_{13} $(\text{ppm } O_3)_{03}$	- - -	d_{1j} $(\text{ppm } O_3)_{oj}$
2. Data processing check (d_{2j})	d_{21}	d_{22}	d_{23}	- - -	d_{2j}

*Data processing errors are corrected when found and are, therefore, not reported as defects.

+This is actually the value of one check while d_{2j} is the average of two checks.

Figure 17: Data Qualification Form

Check values (of d_{1j}) are calculated as directed on page 51 and reported in ppm. The concentration value used for the audit is reported as ppm O_3 for the audit. Values of d_{2j} need be reported only if requested by the Manager. All reported check values exceeding the definition of a defect should be marked for easy recognition by circling on the form. Attach the data qualification form to the SAROAD form and forward for additional internal review or to the user.

SUGGESTED STANDARDS FOR JUDGING PERFORMANCE USING AUDIT DATA

Results from various tests of the chemiluminescent method (Ref. 2) show that system precision is a function of the O_3 concentration. The performance standard given in Table 3 for the measurement of control samples was taken from a collaborative test conducted under controlled conditions and may be too restrictive for field conditions. The value given represents the 3σ limit. This standard should be reevaluated and adjusted for different concentration levels when data collected from the measurement of control samples become available.

COLLECTION OF INFORMATION TO DETECT OR IDENTIFY TROUBLE

In a quality assurance program one of the most effective means of preventing trouble is to respond immediately to reports from the operator of suspicious data or equipment malfunctions. Application of proper corrective actions at this point can reduce or prevent the collection of poor quality data. Important error sources, methods for monitoring applicable variables, and suggested control limits for each source are discussed in this section.

Identification of Important Variables

A great many variables can affect the expected precision and accuracy of measurements made by the chemiluminescent method. Certain of these are related to analysis uncertainties and others to instrument characteristics. Major sources of error are discussed below.

Inaccuracy and Imprecision in the O_3 Output of Ozone Generators (Ref. 3) - There are two components of error involved; one is the reproducibility of the generator itself, and the second is due to the variance associated with the KI Method used in calibrating the generator. It is felt that the day-to-day variation in the generator output will be no greater than the variability of the KI Method.

Imprecision attributable to the KI Method is minimized by replicating the calibration process and constructing an average calibration curve (see page 14). Inaccuracy and imprecision of the ozone generator output may be influenced by variations in line voltage, ambient temperature, and air flow through the generator. There is also some evidence that the generator output decays with time (Ref. 1).

Table 3. SUGGESTED PERFORMANCE STANDARDS

Standards for Defining Defects

1. Measurement of Control Samples; $d_{1j} \geq \pm (0.01 + 0.075 \times \text{ppm}^{*}\ O_3)$

Standard for Correcting Data Processing Errors

2. Data Processing Check; $|d_{2j}| \geq 0.01$ ppm

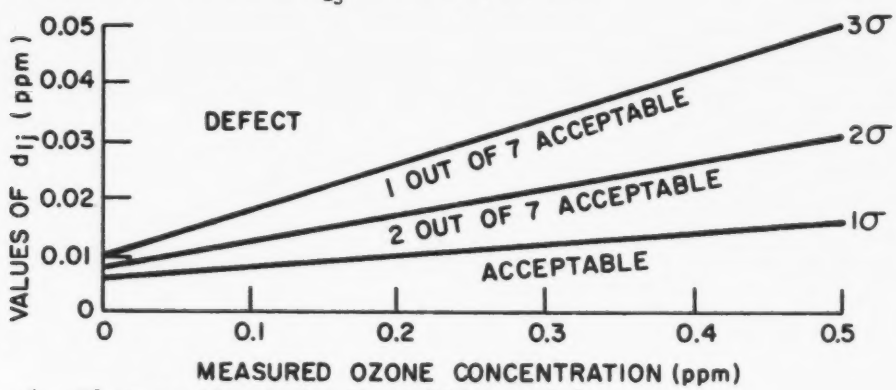
Standards for Audit Rates

3. Suggested minimum auditing rates for data error; number of audits, n=7; lot size, N=100; allowable number of defects per lot, $d^{+} = 0$.

4. Suggested minimum auditing rates for data processing error; number of audits, n=2; lot size, N=24; allowable number of defects (i.e., $|d_{2j}| \geq 0.01$ ppm) per lot, d=0.

Standards for Operation

5. Plot the values of d_{1j} on the graph below.



6. If at any time during the auditing period

   (a) one defect (d=1) is observed (i.e., a plotted value of d_{1j} is in the defect region of the graph),

   (b) two plotted points fall in the region between the 2σ and 3σ lines, or

   (c) four d_{1j} values fall outside the acceptable region;

   increase the audit rate to n=20, N=100 until the cause has been determined and corrected.

7. If at any time two defects (d=2) are observed (i.e., two d_{1j} values plot in the defect region in the same auditing period), stop collecting data until the cause has been determined and corrected.

*ppm O_3 is the concentration measured by the KI Method or the output of the ozone generator.

+An unsubscripted d represents the number of defects observed from n audits of a lot size of N.

Large variations in the output between span calibrations should be detected as a larger than normal span drift. A continuous decay with time would be detected as it approaches the 2σ or 3σ values by the auditing process.

Data Processing Errors - Data processing, starting with reducing the data from a strip chart record through the act of recording the measured concentration on the SAROAD form, is subject to many types of errors. Perhaps the major source of error is in reading hourly averages from the strip chart record. This is a subjective process and even the act of checking a given hourly average does not insure its absolute correctness. The approach used in Section II, page 31 means that one can be about 55% confident that no more than 10% of the reported hourly averages are in error by more than $\pm$ 0.01 ppm.

The magnitude of data processing errors can be estimated from, and controlled by, the auditing program through the performance of periodic checks and making corrections when large errors are detected. A procedure for estimating the bias and standard deviation of processing errors is given in Section IV, page 83.

Zero Drift - Zero drift is defined as the change in instrument output over a stated period of time, usually 24 hours, of unadjusted, continuous operation when the input concentration is zero.

Several variables contribute to zero drift. Some variables such as variations in ambient room temperature, source voltage, and sample or ethylene flow rate result in a zero drift that is not linear with time. Therefore, performing a zero and span calibration does not correct for the component of drift throughout the sampling period but rather just at the time the calibration is performed.

Degradation of electronic components such as the photomultiplier tube may result in a zero drift that is linear with time. Periodic zero and span calibrations allow for correction of this component of zero drift for the entire sampling period.

The importance of zero drift to data quality can be determined from the results obtained from measuring control samples. If a zero and span calibration is nearly always required in order to measure a control sample within desired limits (see page 51), a zero drift check as described on page 34 should be performed to determine the characteristics and major causes of the drift. For a drift that is generally linear with time, it is valid to perform a zero and span before measuring control samples as part of the auditing process. However, if the drift is a function of variations in temperature, voltage, or pressure, as can be determined by the special checks in Section II, starting on page 34, zero and span calibrations should not be performed before measuring control samples for auditing purposes. In this case meeting desired performance standards may require more frequent zero and span calibrations or more rigid control of temperature, voltage, and pressure, as appropriate.

Span Drift - Span drift is defined as the change in instrument output over a stated time period of unadjusted, continuous operation when the input concentration is a stated upscale value. For most chemiluminescent analyzers one component of span drift is zero drift and is corrected or controlled as discussed above. The component of span drift other than zero drift can be caused by electronic defects or an apparent drift can result from a change in the generator output. If this component of span drift is large or shows a continuous increase with time, the manufacturer's manual should be followed for troubleshooting and correction of the defect. The importance or magnitude of span drift can be determined from the zero and span calibrations after each sampling period.

Excessive Noise - Noise is defined as spontaneous deviations from a mean output not caused by input concentration changes. Excessive noise may result when an analyzer is exposed to mechanical vibrations. Other sources of noise include a high gain setting on the recorder, accumulation of dirt on the detector cell walls and window, loose dirt in the detector cell, and the inherent noise of the detector photomultiplier and associated electronics. The latter source of noise can be minimized by electronically damping the photomultiplier output signal.

Excessive noise is evidenced by either an extra broad strip chart trace or a narrow but erratic trace. The manufacturer's manual should be followed for troubleshooting and correcting the cause.

Flow Rate - Analyzer response is sensitive in varying degrees to ethylene flow and to sample air flow (Refs. 4 and 5). At an ethylene flow rate of 30 mℓ/min analyzer response showed a maximum at a sample air flow rate of approximately 1 ℓ/min. Response decreases for sample air flow-rate variations above or below this value (Ref. 4). The ethylene flow rate is not critical for a sample air flow rate of 1 ℓ/min showing only a 30 percent change in output current for a factor of three change in ethylene flow rate.

Calibration results are affected by variations in the air flow rate through the generator. Use of a flow controller as recommended in the reference method minimizes the effect of this source of error.

Flow-rate variations should be detected by the operational checks performed before and after each sampling period, by the results of zero and span calibrations performed before and after each sampling period, or by the audit checks performed 7 times every 100 sampling periods.

How to Monitor Important Variables

System noise, zero drift, span drift, and flow rates are monitored as part of the routine operating procedures. Implementing an auditing program effectively monitors long-term variations in generator output, and data processing errors. Variations in ambient room temperature and/or source voltage can be monitored with a minimum-maximum thermometer and an a.c. voltmeter, respectively. Table 4 summarizes the variables and how they can be monitored.

Table 4. METHODS OF MONITORING VARIABLES

Variable	Method of monitoring
1. Ozone generator output	Measurement of control samples as part of the auditing program, and measurement of span drift before and after each sampling period.
2. Flow rate	Routine operational checks of ethylene flow and sample air flow before and after each sampling period.
3. Data processing errors	Data processing checks performed as a part of the auditing program.
4. Zero drift	Zero check and adjustment before each sampling period as part of routine operating procedure.
5. Span drift	Span check and adjustment before each sampling period as part of routine operating procedure.
6. System noise	Check of strip chart record trace for signs of noise after each sampling period as part of routine operating procedure.
7. Temperature variation	Minimum-maximum thermometer placed near the analyzer, or any other temperature-indicating device, read periodically throughout the sampling period. This would usually be done as a special check.
8. Voltage variation	A.C. voltmeter measuring the voltage to the analyzer and read periodically throughout the sampling period. This would usually be done as a special check.

Suggested Control Limits

Appropriate control limits for individual variables will depend on the level of performance needed. Table 5 gives suggested performance standards for measuring control samples. The standards are given in terms of a mean (bias) and standard deviation.

Standards given for the measurement of control samples were taken from the results of a collaborative test (Ref. 2). The standard deviation, σ_1, is a function of the O_3 concentration and should be reevaluated for different levels as the necessary data become available. The value used here may be too restricted for normal field operations.

In the table, error in measuring control samples has been divided into four components. They are: 1) error in generator output, 2) zero drift, 3) span drift, and 4) noise. The values given for the various error components were arrived at in the following way. Short-term tests of the ozone generator of thirty minutes duration showed variation of about or less than 1 percent (at the 1σ level) for two levels of output (Ref. 3). Also, long-term drifts will be detected by a trend in the span calibration data for drifts as large as 6 or 7 percent of the original value. Therefore, it is felt that with proper monitoring and auditing, variations in the generator output can be detected and maintained at a level of $\pm$ 2 percent (1σ) of the average value.

The nonlinear component of zero drift which can result from variations in temperature, pressure, or voltage is not totally corrected for by zero and span calibrations. If the zero drift is randomly positive and negative from sampling period to sampling period, the drift probably has a large nonlinear component. From previous experience with chemiluminescent analyzers, a $\pm$ 0.01 ppm nonlinear zero drift over a 24-hour sampling period is believed to be a reasonable upper limit.

The effect of span drift, that component other than zero drift, is a function of the O_3 concentration level being measured. This component of drift is normally small and is usually measured at about 80 percent of full scale. The effect, then, in this case would be the ratio of the O_3 concentration being measured and 0.4 ppm (80 percent of scale for a range of 0 to 0.5 ppm) times the span drift in ppm. It is estimated that this component of drift very seldom introduces an error larger than $\pm$ 0.01 ppm and on the average accounts for less than $\pm$ 0.001 ppm error in the measured value.

System noise can originate in the analyzer or recorder. Specifications on most analyzers quote a maximum noise level of $\pm$ 1 percent of full scale or $\pm$ 0.005 ppm for a 0 to 0.5 ppm scale. With proper maintenance the combined noise levels of analyzer and recorder should seldom exceed an equivalent concentration of $\pm$ 0.01 ppm.

Table 5. SUGGESTED CONTROL LIMITS FOR PARAMETERS AND/OR VARIABLES

Parameter/Variable	Suggested Performance Standard		
	Mean	Standard Deviation (ppm)	Upper Limit (3σ)
Measurement of control samples	$\bar{d}_1=0$	$\sigma_1=(0.0033+0.025\times\text{ppm } O_3^*)$ $\sigma_1=0.0058^+$	0.0175
(1) Generator output concentration error	$\bar{d}_a=0$	$\sigma_a=0.02$ ppm O_3 $= 0.002$	$\pm$ 0.006
(2) Zero drift (non-linear component) Temperature variations Voltage variations Flow-rate variations	$\bar{d}_b=0$	$\sigma_b=0.0033$	$\pm$ 0.01
(3) Span drift (other than zero drift)	$\bar{d}_c=0$	$\sigma_c=0.0033$	$\pm$ 0.01
(4) Noise	$\bar{d}_d=0$	$\sigma_d=0.0033$	$\pm$ 0.01
Total: $\sigma_1' = \sqrt{\sigma_a^2 + \sigma_b^2 + \sigma_c^2 + \sigma_d^2}$	$\bar{d}_1'=0$	$\sigma_1'=.0061$	$\pm$ 0.0183

*ppm O_3 = true concentration

+all calculated values are for a true ozone concentration of 0.1 ppm

Combining the means and standard deviations of component errors as

$$\bar{d}_1' = \bar{d}_a + \bar{d}_b + \bar{d}_c + \bar{d}_d ,$$

and

$$\sigma_1' = \sqrt{\sigma_a^2 + \sigma_b^2 + \sigma_c^2 + \sigma_d^2}$$

shows that at this level of control the suggested performance standard for measuring control samples is satisfied as is evidenced in Table 5 by

$$\bar{d}_1' = \bar{d}_1 = 0$$

and

$$\sigma_1' \simeq \sigma_1 .$$

PROCEDURES FOR IMPROVING DATA QUALITY

Quality control procedures designed to control or adjust data quality may involve a change in equipment or in operating procedures. Table 6 lists some possible procedures for improving data quality. The applicability or necessity of a procedure for a given monitoring situation will have to be determined from results of the auditing process or special checks as performed to identify the important variables. The expected results are given for each procedure in qualitative terms. If quantitative data are available or reasonably good estimates can be made of the expected change in data quality resulting from implementation of each procedure, a graph similar to that in Figure 23, page 88 of the Management Manual can be constructed. The values used in Table 14, page 89, and Figure 23 are assumed and were not derived from actual data.

Equipment and personnel costs are estimated for each procedure. Personnel costs were taken as 5 dollars per hour for operator time and 10 dollars per hour for supervisor time. Equipment costs were prorated over 5 years for continuous monitoring, i.e., sampling 365 days a year. All costs are for a lot size of 100, that is, 100 days of sampling.

A procedure for selecting the appropriate quality control procedure to insure a desired level of data quality is given below:

(1) Specify the desired performance standard, that is, specify the limits within which you want the deviation between the measured and the true concentration to fall a desired percentage of the time. For example, to measure the true ppm O_3 to within $\pm$ (0.007+0.05×ppm O_3)

Table 6. QUALITY CONTROL PROCEDURES OR ACTIONS

Procedure	Description of Action	Expected Results	Costs (Dollars)		
			Equip	Personnel	Total
A0 Reference method	Reference method with procedures given in the Operations Manual performed routinely.	Reported data will exhibit a standard deviation of approximately $(0.0033+0.025\times ppm^{*} O_3)$	0	0	0
A1 Construct an average calibration curve	Replicate the analyzer calibration 5 times over a period of 1 or 2 weeks and use the average of the replicates.	Reduce the imprecision contributable to the KI Method.	0	150	150
A2 Use electrical time constant	Electrically integrate peak concentrations of less than 15-45 seconds duration.	Reduce the data reduction error by eliminating sharp spikes from the strip chart trace.	0	0	0
A3 Shelter temperature control unit	Install a heating/cooling system capable of maintaining ambient room temperature to within $\pm$ 3°C (5°F) of a preset value.	Reduces variation in ozone generator output.	55	20	75
A4 Voltage control	Install a constant voltage regulator capable of maintaining line voltage to within $\pm$ 1% of a preset value for the ozone generator.	Reduce variation in ozone generator output.	15	0	15

* ppm O_3 = true ozone concentration

95 percent of the time, the following performance standards must be satisfied:

$$|\hat{\tau} \pm 2\hat{\sigma}_T| \leq (0.007 + 0.05 \times \text{ppm } O_3).$$

(2) Determine the system's present performance level from the auditing process, as described in Section IV, Data Quality Assessment, of the Management Manual by setting

$$\hat{\tau} = \bar{d}_1 + \bar{d}_2$$

and

$$\hat{\sigma}_T = \sqrt{s_1^2 + s_2^2} \quad .$$

If the relationship of (1) above is satisfied, no control procedures are required.

(3) If the desired performance standard is not specified, identify the major error components.

(4) Select the quality control procedure(s) which will give the desired improvement in data quality at the lowest cost. Figure 23 on page 88 of the Management Manual illustrates a method for accomplishing this.

The relative position of actions on the graph in Figure 23 will differ for different monitoring networks according to type of equipment being used, available personnel, and local costs. Therefore, each network would need to develop its own graph to aid in selecting the control procedure providing the desired data quality at the lowest cost.

PROCEDURES FOR CHANGING THE AUDITING LEVEL TO GIVE THE DESIRED LEVEL OF CONFIDENCE IN THE REPORTED DATA

The auditing process does not in itself change the quality of the reported data. It does provide a means of assessing the data quality. An increased auditing level increases the confidence in the assessment. It also increases the overall cost of data collection.

Various auditing schemes and levels are discussed in Section IV, Auditing Schemes. Numerous parameters must be known or assumed in order to arrive at an optimum auditing level. Therefore, only two decision rules with two levels of auditing each will be discussed here.

For conditions as assumed in Section IV, page 76 of the Management Manual, a study of Figure 21, page 81, gives the following results. These conditions may or may not apply to your operation. They are included here to call attention to a methodology. Local costs must be used for conditions to apply to your operation.

Decision Rule - Accept the Lot as Good If No Defects Are Found (i.e., d=0)

Most Cost Effective Auditing Level - In Figure 21, page 81, the two solid lines are applicable to this decision rule, i.e., d=0. The cost curve has a minimum at n=7 or an auditing level of 7 checks out of 100 sampling periods. From the probability curve it is seen that at this auditing level there is a probability of 0.47 of accepting a lot as good when the lot (for N=100) actually has 10 defects with an associated average cost of 234 dollars per lot.

Auditing Level for Low Probability of Accepting Bad Data - Increasing the auditing level to n=20, using the same curves in Figure 21 as in above, shows a probability of 0.09 of accepting a lot as good when the lot actually has 10 defects. The average cost associated with this level of auditing is approximately 430 dollars per lot.

Decision Rule - Accept the Lot as Good If No More than One (1) Defect is Found (i.e., $d \leq 1$).

Most Cost Effective Auditing Level - From the two dashed curves in Figure 21 it can be seen that the cost curve has a minimum at n=15. At this level of auditing there is a probability of 0.51 of accepting a lot of data as good when it has 10 defects. The average cost per lot is approximately 340 dollars.

Auditing Level for Low Probability of Accepting Bad Data - For an auditing level of n=20 the probability of accepting a lot with 10 percent defects is about 0.36 as read from the $d \leq 1$ probability curve. The average cost per lot is approximately 375 dollars.

It must be realized that the shape of a cost curve is determined by the assumed costs of performing the audit and of reporting bad data. These costs must be determined for individual monitoring situations in order to select optimum auditing levels.

MONITORING STRATEGIES AND COST

Selecting the optimum monitoring strategy in terms of cost and data quality requires a knowledge of the present data quality, major error components, cost of implementing available control procedures, and potential increase in system precision and accuracy.

A methodology for comparing strategies to obtain the desired precision of the data is illustrated in Section IV, page 86. Table 6, page 62, lists control procedures with estimated costs of implementation and expected results in terms of which error component(s) are affected by the control.

Three system configurations identified as best strategies in Figure 23, page 88, of the Management Manual are summarized here. All calculations were made for a true ozone concentration of 0.1 ppm. The relationship of the monitoring strategies will remain the same for all concentration levels. However, the variance in the data is a function of concentration and should be computed for the concentration range of interest.

Reference Method

Description of Method - This refers to a sampling system as illustrated in Figure 2, page 6, of the Operations Manual. Routine operating procedures as given in the Operations Manual are to be followed with special checks performed to identify problem areas when performance standards are not being met. An auditing level of n=7 out of a lot size of N=100 is recommended for this strategy. This strategy is identified as A0 in Table 14 and Figure 23 in the Management Manual.

Costs - Taken as reference or zero cost.

Data Quality - Combining the assumptions made concerning the measurement of control samples and data processing errors, the data quality as read from the graph in Figure 23 shows a standard deviation of 0.0066 ppm. This means that a true ozone concentration of 0.1 ppm would be measured within the limits of 0.0802 ppm and 0.1198 ppm approximately 99.7 percent of the time. To express it another way, one could say that true concentrations close to 0.1 ppm would be measured within $\pm$ 20 percent of the true value approximately 99.7 percent of the time.

Reference Method Plus Actions A1 and A2 (A1+A2)

Description of Method - Identical with the above method except an average calibration curve is constructed from 5 replicates of the calibration curve and a 15 second time constant is used on the photomultiplier output signal to integrate out spikes of less than 15 seconds duration. This reduces the chance of large data reduction errors which can be a highly subjective process in the measurement method.

Costs - Estimated average cost per lot in excess of the costs of the reference method above is 150 dollars.

Data Quality - From Table 14 and Figure 23 the data quality would be described by a standard deviation of 0.0051 ppm. This means that concentrations near 0.1 ppm will be measured within about $\pm$ 15 percent of the true value 99.7 percent of the time.

Reference Method Plus Actions A1, A2, A3, and A4 (A6)

Description of Method - Identical to the immediate above method with the addition of operating the analyzer in a shelter where the temperature is controlled to within ± 3°C of a set value and utilizing a constant voltage regulator in the power line to the analyzer.

Costs - From Figure 23 it is seen that the average cost per lot of data in excess of the cost of the reference method is about 240 dollars.

Data Quality - The combination of all the actions as shown in Figure 23 has a standard deviation of about 0.0040 ppm (for a true concentration of 0.1 ppm). This means that ozone concentrations near 0.1 ppm will be measured within ± 12 percent of the true value approximately 99.7 percent of the time.

For these assumed values and conditions the data quality as measured by the standard deviation has improved by 40 percent (i.e., the standard deviation has decreased by 40 percent) in going from Action A0 to Action A6 at an average additional cost of 240 dollars per lot of 100 samples.

MANAGEMENT MANUAL

GENERAL

The objectives of a data quality assurance program for the Chemiluminescent Method of measuring the concentration of ozone (ppm O_3) in the ambient air were given in Section I. In this part of the document, procedures will be given to assist the manager in making decisions pertaining to data quality based on the checking and auditing procedures described in Sections II and III. These procedures can be employed to:

(1) determine the extent of independent auditing to be performed,

(2) detect when the data quality is inadequate,

(3) assess overall data quality,

(4) relate costs of data quality assurance procedures to a measure of data quality, and to

(5) select from the options available to the manager the alternative(s) which will enable him to meet the data quality goals by the most cost-effective means.

The determination of the extent of auditing is considered in the section entitled AUDITING SCHEMES. Objectives 2 and 3 are discussed in the section entitled DATA QUALITY ASSESSMENT, page 82. Finally, Objectives 4 and 5 above are described in the section entitled DATA QUALITY VS COST OF IMPLEMENTING ACTIONS, page 86. The cost data are assumed and a methodology provided. When better cost data become available, improvements can be made in the management decisions.

If the current reference system is providing data quality consistent with that required by the user, there will be no need to alter the physical system or to increase the auditing level. In fact several detailed procedures could be bypassed if continuing satisfactory data quality is implied by the audit. However, if the data quality is not adequate, e.g., either a large bias and/or imprecision exists in the reported data, then (1) increased auditing should be employed, (2) the assignable cause determined, and (3) the system deficiency corrected. The correction can take the form of a change in the operating procedure, e.g., use an average of five calibrations with the KI method to construct an average calibration curve; or it may be a change in equipment such as the installation of an improved temperature control system. An increase in the auditing level will increase the confidence in the reported measure of precision/bias and aid in identifying the assignable cause(s) of the large deviations. The level of auditing will be considered in the following subsection.

The audit procedure and the reported results can serve a two fold purpose. They can be used to (1) screen the data, by lots of say N = 50 or 100, to detect when the data quality may be inadequate, and (2) calculate the bias and precision of the audited measurement and hence estimate the bias/precision of the final reported concentration of ozone in the ambient air. In order to perform (1), suggested standards are provided for use in comparing the audited results with the reported values and a defect is defined in terms of the standards. This approach requires only the reporting of the number of defects in the n auditing checks. In the second method above, it is required to report the measures of bias/precision in the audits. These values are then used in assessing the overall data quality. Approach (1) is suggested as a beginning step even though it will not make maximum use of the data collected in the auditing program. The simplicity of the approach and the explicit definition of a defect will aid in its implementation. After experience has been gained in using the auditing scheme and in reporting and calculating the results, it is recommended that approach (2) be implemented.

It is important that the audit procedure be independent of previously reported results and be a true check of the system under normal operating procedures. Independence can be achieved, for example, by providing a control sample of unknown concentration (i.e., randomly setting the generator sleeve position) to the operator and requesting that he measure and report the concentration of the sample. To insure that the check is made under normal operating procedures, it is required that the audit be performed without any special check of the system prior to the audit other than that usually performed during each sampling period.

AUDITING SCHEMES

Auditing a measurement process costs time and money. On the other hand, reporting poor quality data can also be very costly. For example, the reported data might be used to determine a relationship between health damage and concentrations of certain pollutants. If poor quality data are reported, it is possible that invalid inferences or standards derived from the data will cost many dollars. These implications may be unknown to the manager until some report is provided to him referencing his data; hence the importance of reporting the precision and bias with the data.

Considering the cost of reporting poor quality data, it is desirable to perform the necessary audits to assess the data quality and to invalidate unsatisfactory data with high probability. On the other hand, if the data quality is satisfactory, an auditing scheme will only increase the data measurement and processing cost. An appropriate tradeoff or balance of these costs must be sought. These costs are discussed under Cost Relationships.

Now consider the implication of an auditing scheme to determine or judge the quality of the reported data in terms of an acceptance sampling scheme. Let the data be assembled into homogeneous lots of N = 50 or 100 sampling periods. Suppose that n periods are sampled in the

manner suggested in Section III. That is, the N = 50 or 100 sampling periods are subdivided into equal time intervals (as nearly equal as possible); then one day is selected at random during each interval. Figure 18 gives a diagram of the data flow, sampling, and decision making process for an auditing level of n = 7.

Statistics of Various Auditing Schemes

Suppose that the lot size is N = 100 periods (days), that n = 7 periods are selected at random, and that there are 5% defectives in the 100, or 5 defectives. The probability that the sample of 7 contains 0, 1, ..., 5 defectives is given by the following.

$$p(0 \text{ defectives}) = \frac{\binom{5}{0}\binom{95}{7}}{\binom{100}{7}} \quad ,$$

and for d defectives

$$p(d \text{ defectives}) = \frac{\binom{5}{d}\binom{95}{7-9}}{\binom{100}{7}} \quad , \; d \leq 5 \; .$$

The values are tabulated below for d = 0, 1, ..., 6 and for the two data quality levels.

Table 7. P(d defectives)

	Data Quality	
d	D=5% Defectives	D=15% Defectives
0	0.6903	0.3083
1	0.2715	0.4098
2	0.0362	0.2152
3	0.0020	0.0576
5	0.00004	0.0084
6	= 0	≈ 0

Figure 19A gives the probabilities of d = 0 and d ≤ 1 defectives as a function of sample size. The probability is given for lot size N = 100, D = 5 and 15% defectives, for sample sizes (auditing levels) from 1 to 25. For example, if n = 10 measurements are audited and D = 5% defectives,

* $\frac{\binom{5}{0}\binom{95}{7}}{\binom{100}{7}} = \frac{\left(\frac{5!}{0!5!}\right)\left(\frac{95!}{7!88!}\right)}{\left(\frac{100!}{7!93!}\right)} = \frac{95 \cdot 94 \cdots 89}{100 \cdot 99 \cdots 94} = 0.6903.$

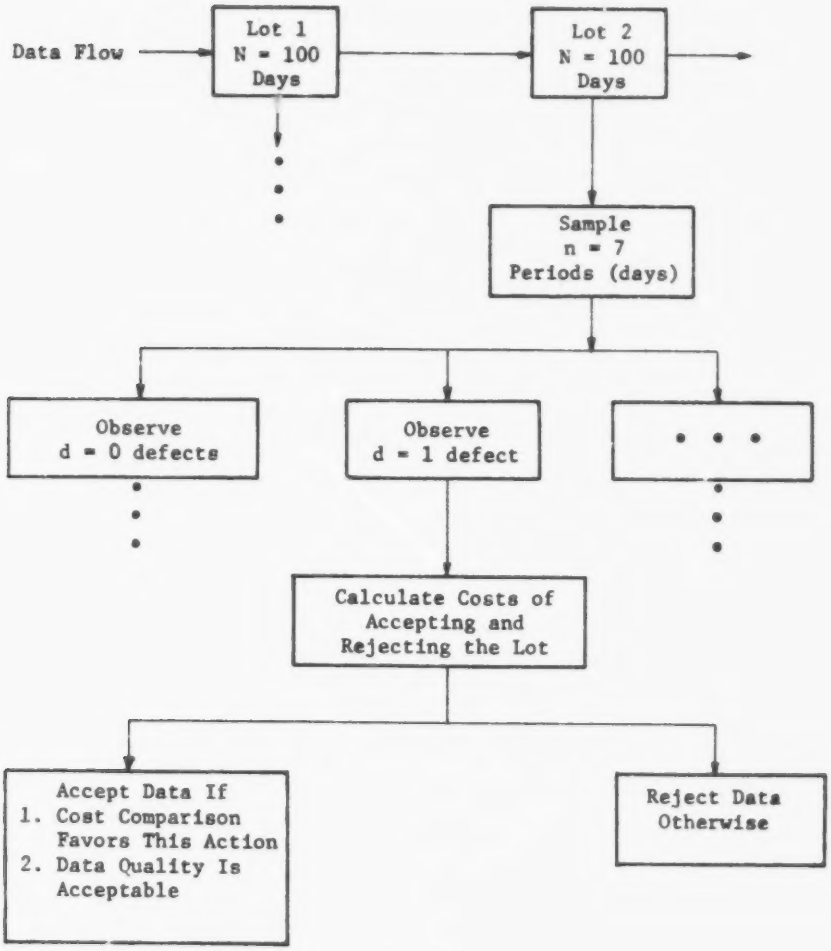


Figure 18: Data Flow Diagram for Auditing Scheme

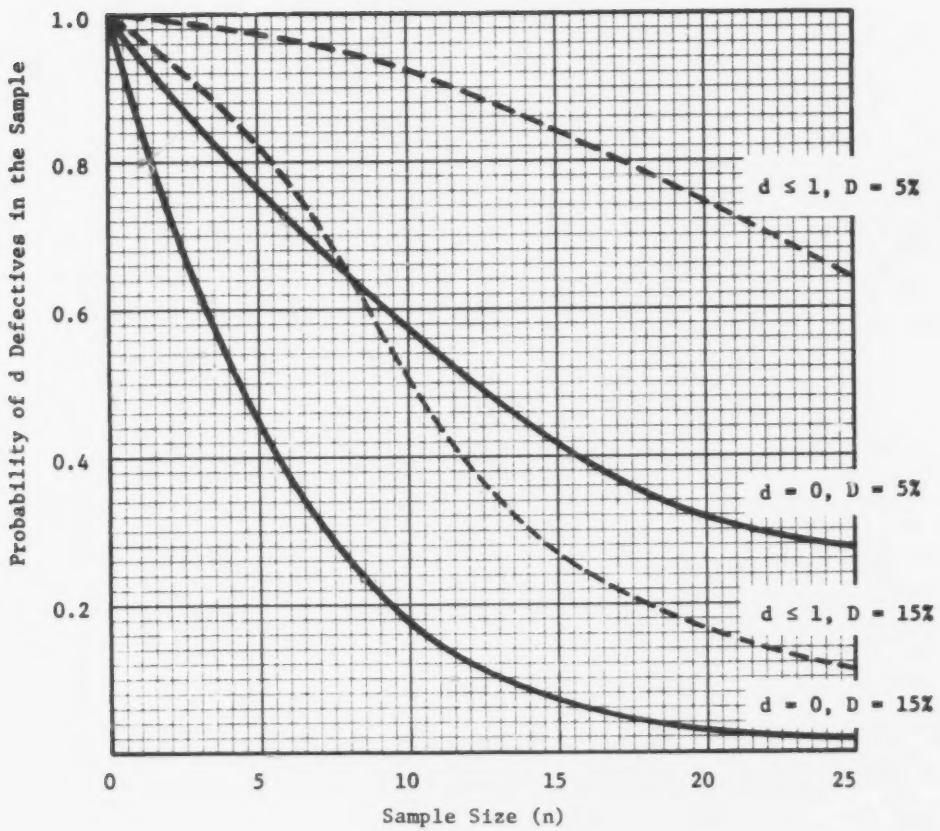


Figure 19A: Probability of d Defectives in the Sample If the Lot (N = 100) Contains D% Defectives

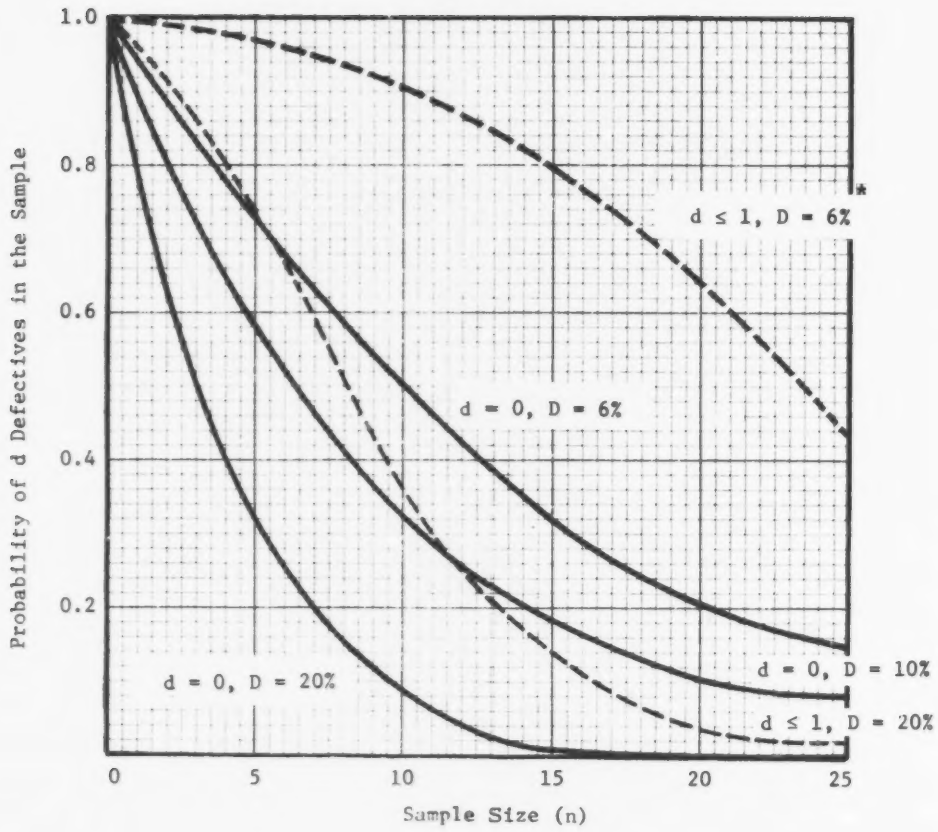


Figure 19B: Probability of d Defectives in the Sample If the Lot (N = 50) Contains D% Defectives.

*This graph is for a lot size of N = 50. Only whole numbers of defectives are physically possible; therefore, even values of D (i.e., 6, 10, and 20 percent) are given rather than the odd values of 5 and 15 percent as given in Figure 19A.

the probability of d = 0 defectives is 0.58. Figure 19B gives the probabilities for lot size N = 50, for D = 6, 10, and 20% defectives, and for d = 0 and d $\leq$ 1. These curves will be used in calculating the cost relationships.

Selecting the Auditing Level

One consideration in determining an auditing level n used in assessing the data quality is to calculate the value of n which for a prescribed level of confidence will imply that the percent of defectives in the lot is less than 10 percent, say, if zero defectives are observed in the sample.* Figures 20A and 20B give the percentage of good measurements in the lot sampled for several levels of confidence, 50, 60, 80, 90, and 95%. The curves in 20A assume that 0 defectives are observed in the sample, and those in 20B that 1 defective is observed in the sample. The solid curves on the figures are based on a lot size of N = 100; two dashed curves are shown in Figure 20A for N = 50; the differences between the corresponding curves are small for the range of sample sizes considered.

For example, for zero defectives in a sample of 7 from a lot of N = 100, one is 50% confident that there are less than 10% defective mesaurements among the 100 reported values. For zero defectives in a sample of 15 from N = 100, one is 90% confident that there are less than 10% defective measurements. Several such values were obtained from Figure 20A and placed in Table 8 below for convenient reference.

Table 8. REQUIRED AUDITING LEVELS n FOR LOT SIZE N = 100 ASSUMING ZERO DEFECTIVES

Confidence Level	D = 10%	15%	20%
50%	7	<5	<5
60%	9	6	<5
80%	15	10	8
90%	20	15	11
95%	$\approx$ 25	18	13

*Obviously, the definition of defective need not always be the same and must be clearly stated each time. The definitions employed herein are based on results of collaborative test programs.

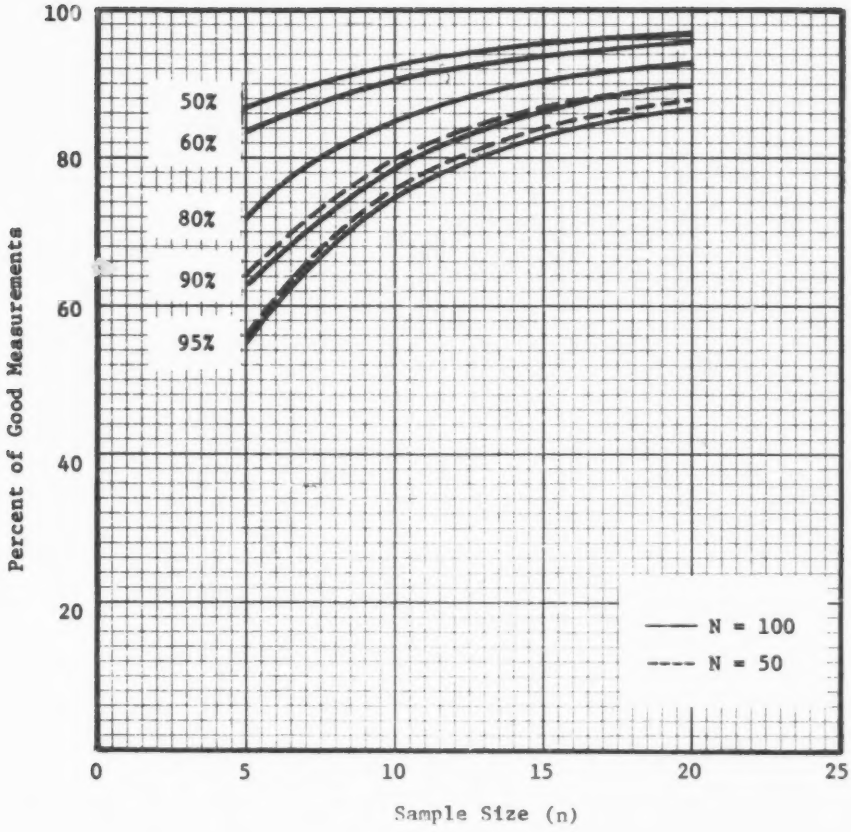


Figure 20A: Percentage of Good Measurements Vs. Sample Size for No Defectives and Indicated Confidence Level

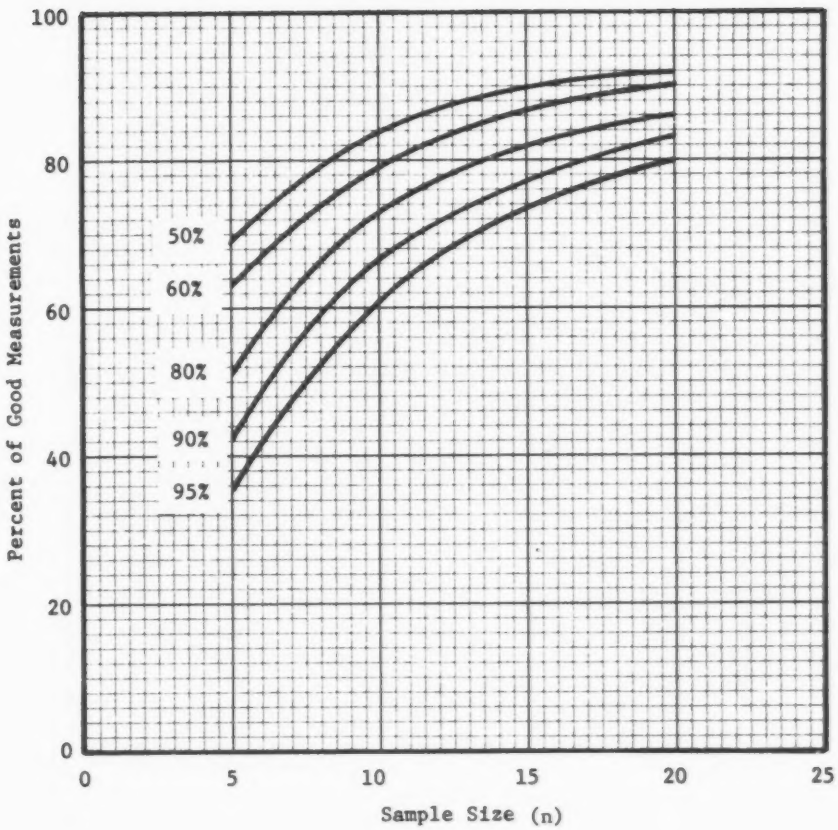


Figure 20B: Percentage of Good Measurements Vs. Sample Size for 1 Defective Observed and Indicated Confidence Level

Lot Size = 100

Cost Relationships

The auditing scheme can be translated into costs using the costs of auditing, rejecting good data, and accepting poor quality data. These costs may be very different in different geographic locations. Therefore, purely for purposes of illustrating a method, the cost of auditing is assumed to be directly proportional to the auditing level. For n = 7 it is assumed to be $155 per lot of 100. The cost of rejecting good quality data is assumed to be $600 for a lot of N = 100. The cost of reporting poor quality data is taken to be $800. To repeat, these costs given in Table 9 are assumed for the purpose of illustrating a methodology of relating auditing costs to data quality. Meaningful results can only be obtained by using correct local information.

Table 9. COSTS VS. DATA QUALITY

	Data Quality	
	"Good"	"Bad"
	D ≤ 10%	D > 10%
	Incorrect Decision	Correct Decision
Reject Lot of Data	Lose cost of performing* audit plus cost of rejecting good quality data. (-$600 - $155)	Lose cost of performing audit, save cost of not permitting poor quality data to be reported. ($400 - $155)
	Correct Decision	Incorrect Decision
Accept Lot of Data	Lose cost of performing audit. (-$155)	Lose cost of performing audit plus cost of declaring poor quality data valid. (-$800 - $155)

Suppose that 50 percent of the lots have more than 10 percent defectives and 50 percent have less than 10 percent defectives. (The percentage of defective lots can be varied as will be described in the final report under the contract.) For simplicity of calculation, it is further assumed that the good lots have exactly 5 percent defectives and the poor quality lots have 15 percent defectives.

*Cost of performing audit varies with the sample size; it is assumed to be $155 for n = 7 audits per N = 100 lot size.

Suppose that n = 7 measurements out of a lot of N = 100 have been audited and none found to be defective. Furthermore, consider the two possible decisions of rejecting the lot and accepting the lot and the relative costs of each. These results are given in Tables 10A and 10B.

Table 10A. COSTS IF 0 DEFECTIVES ARE OBSERVED AND THE LOT IS REJECTED

		Correct Decision	Incorrect Decision	Net Value ($)
Reject Lot	D = 5%	---	$p_1 = 0.69$ $C_1 = -600 - 155$	$p_1C_1 = -\$521$
	D = 15%	$p_2 = 0.31$ $C_2 = 400 - 155$	---	$p_2C_2 = \$76$

$$\text{Cost} = p_1C_1 + p_2C_2 = -\$445$$

Table 10B. COSTS IF 0 DEFECTIVES ARE OBSERVED AND THE LOT IS ACCEPTED

		Correct Decision	Incorrect Decision	Net Value ($)
Accept Lot	D = 5%	$p_1 = 0.69$ $C_3 = -155$	--- ---	$p_1C_3 = -\$107$
	D = 15%	---	$p_2 = 0.31$ $C_4 = -800 - 155$	$p_2C_4 = -\$296$

$$\text{Cost} = p_1C_3 + p_2C_4 = -\$403$$

The value p_1 (p_2) in the above table is the probability that the lot is 5% (15%) defective given that 0 defectives have been observed. For example,

$$p_1 = \frac{\left(\begin{array}{c}\text{probability that the lot is 5\% defective} \\ \underline{\text{and}}\ 0\ \text{defectives are observed}\end{array}\right)}{p\left(\begin{array}{c}\text{lot is 5\% defective } \underline{\text{and}} \\ 0\ \text{defectives observed}\end{array}\right) + p\left(\begin{array}{c}\text{lot is 15\% defective } \underline{\text{and}} \\ 0\ \text{defectives observed}\end{array}\right)}$$

$$= \frac{0.5(0.69)}{0.5(0.69) + 0.5(0.31)} = 0.69 .$$

$$p_2 = \frac{\left(\begin{array}{c}\text{probability that the lot is 15\% defective} \\ \underline{\text{and}}\ 0\ \text{defectives are observed}\end{array}\right)}{p\left(\begin{array}{c}\text{lot is 5\% defective } \underline{\text{and}} \\ 0\ \text{defectives observed}\end{array}\right) + p\left(\begin{array}{c}\text{lot is 15\% defective } \underline{\text{and}} \\ 0\ \text{defectives observed}\end{array}\right)}$$

$$= \frac{0.5(0.31)}{0.5(0.31) + 0.5(0.69)} = 0.31 .$$

It was assumed that the probability that the lot is 5% defective is 0.5. The probability of observing zero defectives, given the lot quality is 5% or 15%, can be read from the graph of Figure 19A.

A similar table can be constructed for 1, 2, ..., defectives and the net costs determined. The net costs are tabulated in Table 11 for 1, 2, and 3 defectives. The resulting costs indicate that the decision preferred from a purely monetary viewpoint is to accept the lot if 0 defectives are observed and to reject it otherwise. The decision cannot be made on this basis alone. The details of the audit scheme also affect the confidence which can be placed in the data qualification; consideration must be given to that aspect as well as to cost.

Table 11. COSTS IN DOLLARS

Decision	d = number of defectives			
	0	1	2	3
Reject Lot	-445	-155	+101	+207
Accept Lot	-403	-635	-839	-928

Cost Versus Audit Level

After the decision criteria have been selected, an average cost can be calculated. Based on the results of Table 11, the decision criterion is to accept the lot if d = 0 defectives are observed and to reject the lot if d = 1 or more defectives are observed. All the assumptions of the previous section are retained. The auditing level is later varied to obtain the data in Figure 21.

One example calculation is given below and summarized in Table 12. The four cells of Table 12 consider all the possible situations which can occur, i.e., the lots may be bad or good and the decision can be to either accept or reject the lot based on the rule indicated by Table 11. The costs are exactly as indicated in Tables 10A and 10B. The probabilities are computed as follows.

q_1 = (prob. that the lot is 5% defective and 1 or more defects are obtained in the sample)

= (prob. that the lot is 5% defective)(prob. 1 or more defectives are obtained in the sample given the lot is 5% defective)

= 0.5 (0.31) = 0.155

Similarly q_2, q_3, and q_4 in Table 12 are obtained as indicated below.

q_2 = 0.5 (0.69) = 0.345

q_3 = 0.5 (0.69) = 0.345

q_4 = 0.5 (0.31) = 0.155

The sum of all the q's must be unity as all possibilities are considered. The value of 0.5 in each equation is the assumed proportion of good lots (or poor quality lots). The values of 0.31 and 0.69 are the conditional probabilities that given the quality of the lot, either d = 0 or d = 1 or more defectives are observed in the sample. Further details of the computation are given in the final report of this contract.

Table 12. OVERALL AVERAGE COSTS FOR ONE ACCEPTANCE - REJECTION SCHEME

Decision	Good Lots D = 5%	Bad Lots D = 15%	
Reject any lot of data if 1 or more defects are found.	$q_1 = 0.155$ $C_1 = -\$755$	$q_2 = 0.345$ $C_2 = \$245$	$q_1C_1 + q_2C_2 = -\$ 32$
Accept any lot of data if 0 defects are found.	$q_3 = 0.345$ $C_3 = -\$155$	$q_4 = 0.155$ $C_4 = -\$955$	$q_3C_3 + q_4C_4 = -\$202$

Average Cost = -$234

In order to interpret the concept of average cost, consider a large number of data lots coming through the system; a decision will be made on each lot in accordance with the above, and a resulting cost of the decision will be determined. For a given lot, the cost may be any one of the four costs, and the proportion of lots with each cost is given by the q's. Hence the overall average cost is given by the sum of the product of q's by the corresponding C's.

In order to relate the average cost as given in Table 12 to the costs given in Table 11, it is necessary to weight the costs in Table 11 by the relative frequency of occurrence of each observed number of defectives, i.e., prob(d). This calculation is made below.

No. of Defectives	Decision Rule	Costs ($) from Table 11	Prob(d)	Cost × Prob(d)
d = 0	Accept	- 403	0.50	-$201.5
1	Reject	- 155	0.34	- 52.7
2	Reject	101	0.1255	12.6
3	Reject	207	0.030	6.2
4	Reject	244	0.0042	1.0
		Totals	0.9997	-$234.4

Thus the value -$234 is the average cost of Table 12 and the weighted average of the costs of Table 11. The weights, Prob(d), are obtained as follows:

Prob(d=0) = Prob(lot is good and d=0 defectives are observed)

+ Prob(lot is poor quality and d=0 defectives are observed)

= 0.5(0.69) + 0.5(0.31) = 0.50 .

This is the proportion of all lots which will have exactly 0 defectives under the assumptions stated. For d = 1, 2, 3, and 4, the values of the probabilities in parentheses above can be read from Table 7.

Based on the stated assumptions, the average cost was determined for several auditing levels as indicated in Table 12. These costs are given in Figure 21. One observes from this figure that n = 7 is cost effective given that one accepts it only if zero defectives are observed. (See curve for d = 0.)

If the lots are accepted if either 0 or 1 defectives are observed, then referring to the curve $d \leq 1$, the best sampling level is n = 15. The curve of probability of $d = 0$ ($d \leq 1$) defectives in a sample of n from a lot of N = 100 measurements, given that there are 10% defectives in the lot, is also given on the same figure.

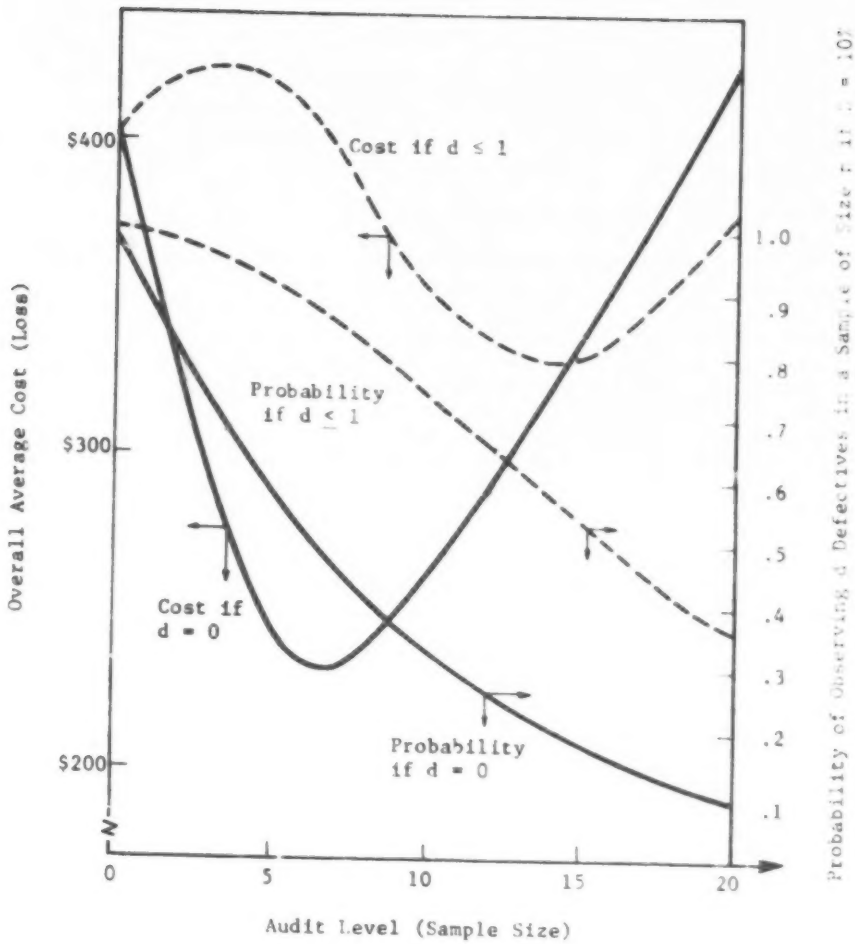


Figure 21: Average Cost Vs. Audit Level
(Lot Size N = 100)

Another alternative is to accept all data without performing an audit. Assuming that one-half (50%) of the lots contain more than 10% defectives, the average cost on a per lot basis would be 0.5(-$800) = -$400. This, however, would preclude qualification of the data. Regardless of cost, it would be an unacceptable alternative.

DATA QUALITY ASSESSMENT

In this section, approach 2 is considered; that is, the precisions and biases of the individual measurements and operational procedures are estimated. These results are then used to make an overall assessment of the data quality.

Assessment of Individual Measurements

Assume for convenience that an auditing period consists of N = 100 days (or sampling periods). Subdivide the auditing period into n equal or nearly equal periods. Make one audit during each period and compute the deviations (differences) between the audit values and the stated values (or previously determined values as measured by the operator) as indicated in the Supervision Manual. For example, if seven audits (n = 7) are to be performed over 100 sampling periods (N = 100), the 100 periods can be subdivided into 7 intervals (6 with 14 periods and 1 with 16 periods). Select one day at random within each interval and perform the suggested audits. The operator should not be aware of when the checks are to be performed.

In order to assess the data quality using measures of bias/precision, the checks are to be combined for the selected auditing period, and the mean difference or bias and the standard deviation of the differences are to be computed as indicated below.

The formulas for average bias and the estimated standard deviations are the standard ones given in statistical texts (e.g., see Ref. 6). The level of sampling or auditing, n, will be considered as a parameter to be selected by the manager to assess the quality of data as required.

(1) Control Sample

$$\text{Bias} = \bar{d}_1 = \frac{\sum_{j=1}^{n} d_{1j}}{n},$$

where

d_{1j} = difference in generator output and analyzer response in ppm (see page 51).

$$\text{Standard Deviation} = s_1 = \sqrt{\frac{\Sigma(d_{1j} - \bar{d}_1)^2}{2(n-1)}} \; *$$

where

$\bar{d}_1$ = the average bias, and

s_1 = the estimated standard deviation of the KI (or chemiluminescent) method corrected for the average bias $\bar{d}_1$.

(2) Data Processing Check

$$\text{Bias} = \bar{d}_2 = \frac{\sum_{j=1}^{n} d_{2j}}{n} ,$$

where

d_{2j} = deviation of the concentration of ozone as read from the strip chart, calibration table, and recorded by the operator and by one performing the audit,

$$\text{Standard Deviation} = s_2 = \sqrt{\frac{\sum (d_{2j} - \bar{d}_2)^2}{n-1}}$$

Individual checks on the standard deviations of the two audits can be made by computing the ratio of the estimated standard deviation, s_1, to the corresponding suggested performance standard, σ_1, given in Table 13. If this ratio exceeds values given in Table 13 for any one of the audits, it would indicate that the source of trouble may be assigned to that particular aspect of the measurement process. Critical values of this ratio are given in Figure 22 as a function of sample size and two levels of confidence. Having assessed the general problem area, one then needs to perform the appropriate quality control checks to determine the specific causes of the large deviations.

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*The factor 2 is inserted in the denominator to account for the fact that the variance of the difference of two measurements, each with the same variance, is twice the variance of an individual measurement. The assumption that the two measurements have the same variances is reasonable on the basis of in-house studies. An analysis of these results is given in the final report of this contract.

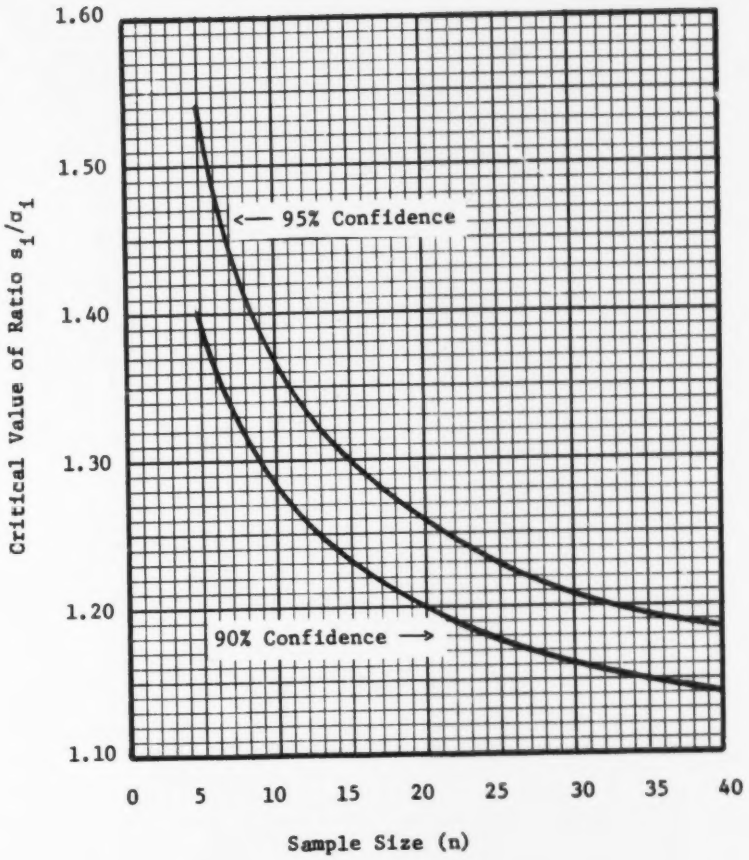

Figure 22: Critical Values of Ratio s_i/σ_i Vs. n

Table 13. CRITICAL VALUES OF s_i/σ_i

Level of Confidence	Statistic	Audit Level				
		n=5	n=10	n=15	n=20	n=25
90%	s_i/σ_i	1.40	1.29	1.23	1.20	1.18
95%	s_i/σ_i	1.54	1.37	1.30	1.26	1.23

s_i = estimated standard deviation

σ_i = hypothesized or suggested standard deviation.

Audit	Suggested Performance Standard
Control Sample	σ_1 = (0.0033+0.025×ppm O_3)
Data Processing Check	σ_2 = 0.003 ppm O_3
Overall Standard Deviation	σ_T = 0.0066 ppm O_3 *

*σ_T is calculated for 0.10 ppm O_3.

Overall Assessment of Data Quality

The values $\bar{d}_1$, $\bar{d}_2$, s_1, and s_2 above measure the bias and variation of the reported data for the two audits. These measures can now be combined to obtain an overall bias estimate $\hat{\tau}$ and standard deviation $\hat{\sigma}_T$, as follows:

$$\hat{\tau} = \bar{d}_1 + \bar{d}_2$$

$$\hat{\sigma}_T = \sqrt{s_1^2 + s_2^2} \quad .$$

These estimates can then be used in reporting the overall bias and precision as suggested by the following. The true concentration of ozone should fall in the following interval where ppm O_3 is the measured concentration,

$$\text{ppm } O_3 + \hat{\tau} \pm 2\hat{\sigma}_T \quad ,$$

approximately 95 percent of the time, or within the interval

$$\text{ppm } O_3 + \hat{\tau} \pm 3\hat{\sigma}_T ,$$

approximately 99.7 percent of the time. When computed from audit data, the value $2\hat{\sigma}_T$ (or $3\hat{\sigma}_T$) is actually dependent on the number of audits conducted. If n is large, say about 25 or larger, the value 2 (or 3) is appropriate.

In reporting the data quality, the bias, overall standard deviation, and auditing level should be reported in an ideal situation (see the section entitled DATA PRESENTATION for further discussion). More restricted information following approach 1 is suggested in the Supervision Manual as a minimal reporting procedure.

If the overall reported precisions/biases of the data meet or satisfy the requirements of the user of the data, then a reduced auditing level may be employed; on the other hand, if the data quality is not adequate, assignable causes of large deviations should be determined and appropriate action taken to correct the deficiencies. This determination may require increased checking or auditing of the measurement process as well as the performance of certain quality control checks, e.g., monitoring of temperature variations over the 24-hour sampling period.

DATA QUALITY VERSUS COST OF IMPLEMENTING ACTIONS

The discussion and methodology given in a previous section were concerned with the auditing scheme (i.e., level of audit or sample size, costs associated with the data quality, etc.). Increasing the level of audit of the measurement process does not by itself change the quality of the data, but it does increase the information about the quality of the reported data. Hence, fewer good lots will be rejected and more poor quality data will be rejected. If the results of the audit imply that certain process measurement variables or operational procedures are major contributors to the total error or variation in the reported concentration of ozone, then alternative strategies for reducing these variations need to be investigated. This section illustrate a methodology for comparing the strategies to obtain the desired precision of the data. In practice it would be necessary to experiment with one or more strategies, to determine the potential increase in precision, and to relate the precisions to the relative costs as indicated herein. Several strategies are considered, but only a few of the least costly ones would be acceptable, as illustrated in Figure 23. The assumed values of the standard deviations and biases for each type audit are not based on actual data, except for the reference method. In this case values were taken from Environmental Protection Agency in-house studies. These values are probably smaller than those experienced in the field.

Several alternative actions or strategies can be taken to increase the precision of the reported data. For example, if the temperature variations are large, the measurement methods may vary and, cause variation in ppm O_3. Under these conditions additional control equipment for temperature variation can reduce the variation of the measured responses by calculated amounts and thus reduce the error of the reported concentrations. In this manner, the cost of the added controls can be related to the data quality as measured by the estimated bias/precision of the reported results.

In order to determine a cost efficient procedure, it is necessary to estimate the variance for each source of error (or variation) for each strategy and then to select the strategy or combination of strategies which yields the desired precision with minimum cost. These calculations are summarized in Table 14 with assumed costs of equipment and control procedures.

Suppose that it is desired to make a statement that the true O_3 concentration is within 0.012 of the measured concentration (for simplicity of discussion all calculations were made at a true concentration of 0.1 ppm) with approximately 95 percent confidence. Minimal cost control equipment and checking procedures are to be employed to attain this desired precision.

Examining the graph in Figure 23 of cost versus precision, one observes that A2 is the least costly strategy that meets the required goal of $2\sigma_T = 0.012$ or $\sigma_T = 0.006$ ppm O_3 in the reported concentration. Similarly the combination of A1 and A2 meets the requirement that $3\sigma_T = 0.0153$ or $\sigma_T = 0.0051$ ppm O_3. The assumed values of the standard deviations of the measured concentrations of ozone for the alternative courses of action are given in Table 14. The costs for the various alternatives are given in Table 6 of Section III and in Table 14.

Suppose that it is desired that σ_T be less than 0.005 and that the cost of reporting poor quality data increases rapidly for σ_T greater than 0.005. This assumption is illustrated by the cost curve given by the solid line in Figure 23. For any alternative strategy, the cost of reporting poor quality data is given by the ordinate of this curve corresponding to the strategy.

DATA PRESENTATION

A reported value whose precision and accuracy (bias) are unknown is of little, if any, worth. The actual error of a reported value--that is, the magnitude and sign of its deviation from the true value--is usually unknown. Limits to this error, however, can usually be inferred, with some risk of being incorrect, from the precision of the measurement process by which the reported value was obtained and from reasonable limits to the possible bias of the measurement process. The bias, or systematic error, of a measurement process is the magnitude and direction of its tendency to measure something other than what was intended; its precision refers to the closeness or dispersion of successive independent measurements generated by repeated applications of the process under specified conditions, and its accuracy is determined by the closeness to the true value characteristic of such measurements.

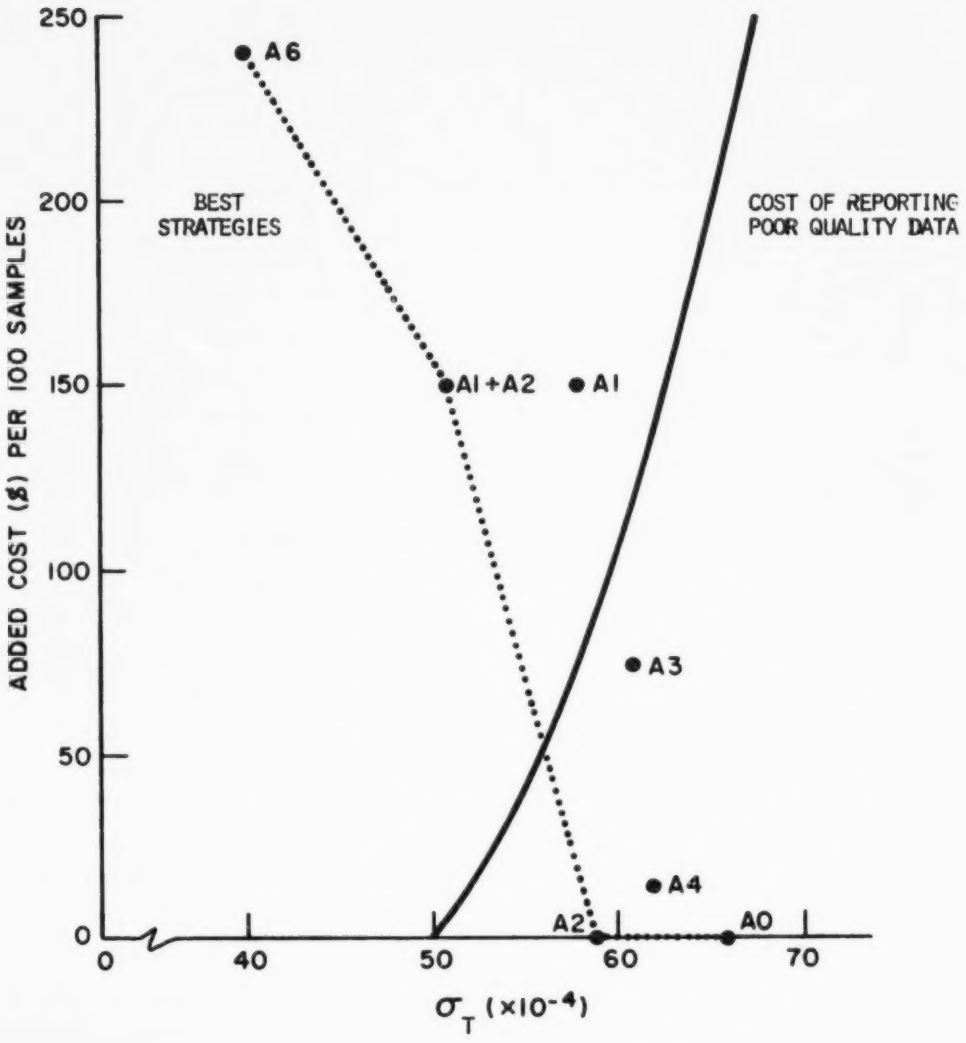

Figure 23. Costs Vs. Precision for Alternative Strategies

Table 14. ASSUMED STANDARD DEVIATIONS FOR ALTERNATIVE STRATEGIES

		A0	A1	A2	A3	A4	. . .	A1+A2	A6*
1. Control Sample	$\bar{d}_1$	0	0	0	0	0		0	0
	σ_1	σ_1	$0.87\sigma_1$	σ_1	$0.92\sigma_1$	$0.93\sigma_1$	. . .	$0.87\sigma_1$	$0.67\sigma_1$
2. Data Processing	$\bar{d}_2$	0	0	0	0	0		0	0
	σ_2	0.003	0.003	0.001	0.003	0.003	. . .	0.001	0.001
**σ_T ppm O_3		0.0066	0.0058	0.0059	0.0061	0.0062	. . .	0.0051	0.0040
***Bias=τ ppm O_3		0	0	0	0	0	. . .	0	0
Added Cost ($)/100 Samples		0	150	0	75	15	. . .	150	240

$\sigma_1 = (0.0033 + 0.025 \times \text{ppm } O_3)$

*A6 = A1 + A2 + A3 + A4

**$\sigma_T^2 = \sigma_1^2 + \sigma_2^2$, $\sigma_T = \sqrt{\sigma_T^2}$ ppm O_3, the σ_T is calculated at 0.10 ppm O_3.

***Bias = $\tau = \bar{d}_1 + \bar{d}_2$, the biases are assumed to be zero for all strategies.

Precision and accuracy are inherent characteristics of the measurement process employed and not of the particular end result obtained. From experience with a particular measurement process and knowledge of its sensitivity to uncontrolled factors, one can often place reasonable bounds on its likely systematic error (bias). This has been done in the model for the measured concentration as indicated in Table 14. It is also necessary to know how well the particular value in hand is likely to agree with other values that the same measurement process might have provided in this instance or might yield on measurements of the same magnitude on another occasion. Such information is provided by the estimated standard deviation of the reported value, which measures (or is an index of) the characteristic disagreement of repeated determinations of the same quantity by the same method and thus serves to indicate the precision (strictly, the imprecision) of the reported value.

A reported result should be qualified by a quasi-absolute type of statement that places bounds on its systematic error and a separate statement of its standard deviation, or of an upper bound thereto, whenever a reliable determination of such value is available. Otherwise, a computed value of the standard deviation should be given together with a statement of the number of degrees of freedom on which it is based.

As an example, consider strategy A0 in Table 14. Here, the assumed standard deviation and bias for true ozone concentration of 0.10 ppm O_3 are $\sigma_T = 0.0066$ and $\tau = 0$, respectively. The results would be reported as the measured concentration, ppm O_3, plus the bias and with the following 2σ limits, along with the audit level and lot size N; e.g.,

$$\text{ppm } O_3 \pm 0.0066,\ n = 7,\ N = 100\ .$$

For concentration other than 0.10 ppm, the overall standard deviation is obtained by

$$\sigma_T = \sqrt{\sigma_1^2 + \sigma_2^2}$$

where σ_1 is given in Table 14, computed at the desired concentration.

PERSONNEL REQUIREMENTS

Personnel requirements as described here are in terms of the chemiluminescent method only. It is realized that these requirements may be only a minor factor in the overall requirements from a systems point of view where several measurement methods are of concern simultaneously.

Training and Experience

Director - The director or one of the professional-level employees should have a basic understanding of statistics as used in quality control. He should be able to perform calculations, such as the mean and standard

deviation, required to define data quality. The importance of and requirements for performing independent and random checks as part of the auditing process must be understood. Three references which treat the above-mentioned topics are listed below:

Probability and Statistics for Engineers, Irvin Miller and John E. Freund, published by Prentice-Hall, Inc., Englewood, N. J., 1965.

Introductory Engineering Statistics, Irwin Guttman and S. S. Wilks, published by John Wiley and Sons, Inc., New York, N. Y., 1965.

The Analysis of Management Decisions, William T. Morris, published by Richard D. Irwin, Inc., Homewood, Illinois, 1964.

Operator - There are or can be two levels of operation involved in the chemiluminescent method.

First, an operator or technician who is involved in the preliminary or initial setup and checkout or is responsible for troubleshooting and repairing the analyzer should have technical training in electronics and/or instrumentation as obtained in a technical or service school or several years of on-the-job experience. For a specific analyzer it would be desirable to have the technician checked out by a manufacturer's representative or at least to have him participate, with the representative, in the initial installation and startup. The manufacturer's instruction book should be available for study or reference by the technician.

Routine operations involve the use of external controls only and require no high-level skills. A high school graduate with proper supervision and on-the-job training can become effective at this level in a very short time.

An effective on-the-job training program could be as follows:

(1) Observe experienced operator perform the different tasks in the measurement process.

(2) Study the operational manual of this document and use it as a guide for performing the operations.

(3) Perform operations under the direct supervision of an experienced operator.

(4) Perform operations independently but with a high level of quality control checks utilizing the technique described in the section on Operator Proficiency Evaluation Procedures below to encourage high quality work.

Another alternative would be to have the operator attend an appropriate basic training course sponsored by EPA.

OPERATOR PROFICIENCY EVALUATION PROCEDURES

One technique which may be useful for early training and qualification of operators is a system of rating the operators as indicated below.

Various types of violations (e.g., invalid sample resulting from operator carelessness, failure to maintain records, use of improper equipment, or calculation error) would be assigned a number of demerits depending upon the relative consequences of the violation. These demerits could then be summed over a fixed period of time of one week, month, etc., and a continuous record maintained. The mean and standard deviation of the number of demerits per week can be determined for each operator and a quality control chart provided for maintaining a record of proficiency of each operator and whether any changes in this level have occurred. In comparing operators, it is necessary to assign demerits on a per unit work load basis in order that the inferences drawn from the chart be consistent. *It is not necessary or desirable for the operator to be aware of this form of evaluation. The supervisor should use it as a means of determining when and what kind of instructions and/or training is needed.*

A sample QC chart is given in Figure 24 below. This chart assumes that the mean and standard deviation of the number of demerits per week, are 5 and 1, respectively. After several operators have been evaluated for a few weeks, the limits can be checked to determine if they are both reasonable and effective in helping to improve and/or maintain the quality of the air quality measurement.

The limits should be based on the operators whose proficiency is average or slightly better than average. Deviations outside the QC limits, either above or below, should be considered in evaluating the operators. Identifying those operators whose proficiency may have improved is just as important as knowing those operators whose proficiency may have decreased.

The above procedure may be extended to an entire monitoring network (system). With appropriate definitions of work load, a continuous record may be maintained of demerits assigned to the system. This procedure might serve as an incentive for teamwork, making suggestions for improved operation procedures, etc.

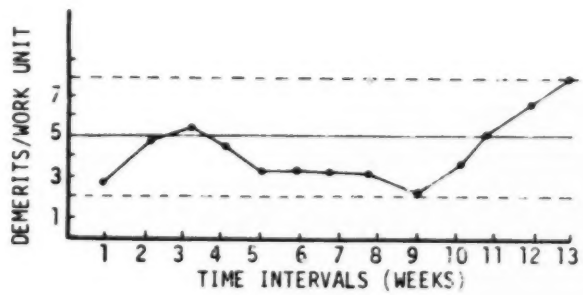

Figure 24: Sample QC Chart for Evaluating Operator Proficiency

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APPENDIX

REFERENCE METHOD FOR THE MEASUREMENT OF PHOTOCHEMICAL OXIDANTS CORRECTED FOR INTERFERENCES DUE TO NITROGEN OXIDES AND SULFUR DIOXIDE

Reproduced from Appendix D, "National Primary and Secondary Ambient Air Quality Standards," *Federal Register*, Vol 36, No. 84, Part II, Friday, April 30, 1971.

APPENDIX D—REFERENCE METHOD FOR THE MEASUREMENT OF PHOTOCHEMICAL OXIDANTS CORRECTED FOR INTERFERENCES DUE TO NITROGEN OXIDES AND SULFUR DIOXIDE

1. *Principle and Applicability.*

1.1 Ambient air and ethylene are delivered simultaneously to a mixing zone where the ozone in the air reacts with the ethylene to emit light which is detected by a photomultiplier tube. The resulting photocurrent is amplified and is either read directly or displayed on a recorder.

1.2 The method is applicable to the continuous measurement of ozone in ambient air.

2. *Range and Sensitivity.*

2.1 The range is 9.8 μg. O_3/m.³ to greater than 1960 μg. O_3/m.³ (0.005 p.p.m. O_3 to greater than 1 p.p.m. O_3).

2.2 The sensitivity is 9.8 μg. O_3/m.³ (0.005 p.p.m. O_3).

3. *Interferences.*

3.1 Other oxidizing and reducing species normally found in ambient air do not interfere.

4. *Precision and Accuracy.*

4.1 The average deviation from the mean of repeated single measurements does not exceed 5 percent of the mean of the measurements.

4.2 The method is accurate within ±7 percent.

5. *Apparatus.*

5.1 *Detector Cell.* Figure D1 is a drawing of a typical detector cell showing flow paths of gases, the mixing zone, and placement of the photomultiplier tube. Other flow paths in which the air and ethylene streams meet at a point near the photomultiplier tube are also suitable.

5.2 *Air Flowmeter.* A device capable of controlling air flows between 0–1.5 l/min.

5.3 *Ethylene Flowmeter.* A device capable of controlling ethylene flows between 0–50 ml./min. At any flow in this range, the device should be capable of maintaining constant flow rate within ±3 ml./min.

5.4 *Air Inlet Filter.* A Teflon filter capable of removing all particles greater than 5 microns in diameter.

5.5 *Photomultiplier Tube.* A high gain low dark current (not more than 1×10^{-9} ampere) photomultiplier tube having its maximum gain at about 430 nm. The following tubes are satisfactory: RCA 4507, RCA 8575, EMI 9750, EMI 9524, and EMI 5506.

5.6 *High Voltage Power Supply.* Capable of delivering up to 2,000 volts of regulated power.

5.7 *Direct Current Amplifier.* Capable of full scale amplification of currents from 10^{-13} to 10^{-9} ampere; an electrometer is commonly used.

5.8 *Recorder.* Capable of full scale display of voltages from the DC amplifier. These voltages commonly are in the 1 millivolt to 1-volt range.

5.9 *Ozone Source and Dilution System.* The ozone source consists of a quartz tube into which ozone-free air is introduced and then irradiated with a very stable low pressure mercury lamp. The level of irradiation is controlled by an adjustable aluminum sleeve which fits around the lamp. Ozone concentrations are varied by adjustment of this sleeve. At a fixed level of irradiation, ozone is produced at a constant rate. By carefully controlling the flow of air through the quartz tube, atmospheres are generated which contain constant concentrations of ozone. The levels of ozone in the test atmospheres are determined by the neutral buffered potassium iodide method (see section 8). This ozone source and dilution system is shown schematically in Figures D2 and D3, and has been described by Hodgeson, Stevens, and Martin.

5.10 *Apparatus for Calibration.*

5.10.1 *Absorber.* All-glass impingers as shown in Figure D4 are recommended. The impingers may be purchased from most major glassware suppliers. Two absorbers in series are needed to insure complete collection of the sample.

5.10.2 *Air Pump.* Capable of drawing 1 liter/minute through the absorbers. The pump should be equipped with a needle valve on the inlet side to regulate flow.

5.10.3 *Thermometer.* With an accuracy of ±2° C.

5.10.4 *Barometer.* Accurate to the nearest mm. Hg.

5.10.5 *Flowmeter.* Calibrated metering device for measuring flow up to 1 liter/minute within ±2 percent. (For measuring flow through impingers.)

5.10.6 *Flowmeter.* For measuring airflow past the lamp; must be capable of measuring flows from 2 to 15 liters/minute within ±5 percent.

5.10.7 *Trap.* Containing glass wool to protect needle valve.

5.10.8 *Volumetric Flasks.* 25, 100, 500, 1,000 ml.

5.10.9 *Buret.* 50 ml.

5.10.10 *Pipets.* 0.5, 1, 2, 3, 4, 10, 25, and 50 ml. volumetric.

5.10.11 *Erlenmeyer Flasks.* 300 ml.

5.10.12 *Spectrophotometer.* Capable of measuring absorbance at 352 nm. Matched 1-cm. cells should be used.

6. *Reagents.*

6.1 *Ethylene.* C. P. grade (minimum).

6.2 *Cylinder Air.* Dry grade.

6.3 *Activated Charcoal Trap.* For filtering cylinder air.

6.4 *Purified Water.* Used for all reagents. To distilled or deionized water in an all-glass distillation apparatus, add a crystal of potassium permanganate and a crystal of barium hydroxide, and redistill.

6.5 *Absorbing Reagent.* Dissolve 13.6 g. potassium dihydrogen phosphate (KH_2PO_4), 14.2 g. anhydrous disodium hydrogen phosphate (Na_2HPO_4) or 35.8 g. dodecahydrate salt ($Na_2HPO_4 12H_2O$), and 10.0 g. potassium iodide (KI) in purified water and dilute to 1,000 ml. The pH should be 6.8±0.2. The solution is stable for several weeks, if stored in a glass-stoppered amber bottle in a cool, dark place.

6.6 *Standard Arsenious Oxide Solution (0.05 N).* Use primary standard grade arsenious oxide (As_2O_3). Dry 1 hour at 105° C. immediately before using. Accurately weigh, to the nearest 0.1 mg., 2.4 g. arsenious oxide from a small glass-stoppered weighing bottle. Dissolve in 25 ml. 1 N sodium hydroxide in a flask or beaker on a steam bath. Add 25 ml. 1 N sulfuric acid. Cool, transfer quantitatively to a 1,000-ml. volumetric flask, and dilute to volume. NOTE: Solution must be neutral to litmus, not alkaline.

$$\text{Normality } As_2O_3 = \frac{\text{wt } As_2O_3 \text{ (g.)}}{49.45}$$

6.7 *Starch Indicator Solution (0.2 percent).* Triturate 0.4 g. soluble starch and approximately 2 mg. mercuric iodide (preservative) with a little water. Add the paste slowly to 200 ml. of boiling water. Continue boiling until the solution is clear, allow to cool, and transfer to a glass-stoppered bottle.

6.8 *Standard Iodine Solution (0.05 N).*

6.8.1 *Preparation.* Dissolve 5.0 g. potassium iodide (KI) and 3.2 g. resublimed iodine (I_2) in 10 ml. purified water. When the iodine dissolves, transfer the solution to a 500-ml. glass-stoppered volumetric flask. Dilute to mark with purified water and mix thoroughly. Keep solution in a dark brown glass-stoppered bottle away from light, and restandardize as necessary.

6.8.2 *Standardization.* Pipet accurately 20 ml. standard arsenious oxide solution into a 300-ml. Erlenmeyer flask. Acidify slightly with 1:10 sulfuric acid, neutralize with solid sodium bicarbonate, and add about 2 g. excess. Titrate with the standard iodine solution using 5 ml. starch solution as indicator. Saturate the solution with carbon dioxide near the end point by adding 1 ml. of 1:10 sulfuric acid. Continue the titration to the first appearance of a blue color which persists for 30 seconds.

$$\text{Normality } I_2 = \frac{\text{ml. } As_2O_3 \times \text{Normality } As_2O_3}{\text{ml. } I_2}$$

6.9 *Diluted Standard Iodine.* Immediately before use, pipet 1 ml. standard iodine solution into a 100-ml. volumetric flask and dilute to volume with absorbing reagent.

7. *Procedure.*

7.1 Instruments can be constructed from the components given here or may be purchased. If commercial instruments are used, follow the specific instructions given in the manufacturer's manual. Calibrate the instrument as directed in section 8. Introduce samples into the system under the same conditions of pressure and flow rate as are used in calibration. By proper adjustments of zero and span controls, direct reading of ozone concentration is possible.

8. *Calibration.*

8.1 *KI Calibration Curve.* Prepare a curve of absorbance of various iodine solutions against calculated ozone equivalents as follows:

8.1.1 Into a series of 25 ml. volumetric flasks, pipet 0.5, 1, 2, 3, and 4 ml. of diluted standard iodine solution (6.9). Dilute each to the mark with absorbing reagent. Mix thoroughly, and immediately read the absorbance of each at 352 nm. against unexposed absorbing reagent as the reference.

8.1.2 Calculate the concentration of the solutions as total $\mu g.\ O_3$ as follows:

$$\text{Total } \mu g.\ O_3 = (N)\,(96)\,(V_1)$$

N = Normality I_2 (see 6.8.2), meq./ml.

V_1 = Volume of diluted standard I_2 added, ml. (0.5, 1, 2, 3, 4).

Plot absorbance versus total $\mu g.\ O_3$.

8.2 *Instrument Calibration.*

8.2.1 *Generation of Test Atmospheres.* Assemble the apparatus as shown in Figure D6. The ozone concentration produced by the generator can be varied by changing the position of the adjustable sleeve. For calibration of ambient air analyzers, the ozone source should be capable of producing ozone concentrations in the range 100 to 1,000 $\mu g./m.^3$ (0.05 to 0.5 p.p.m.) at a flow rate of at least 5 liters per minute. At all times the airflow through the generator must be greater than the total flow required by the sampling systems.

8.2.2 *Sampling and Analyses of Test Atmospheres.* Assemble the KI sampling train as shown in Figure D4. Use ground-glass connections upstream from the impinger. Butt-to-butt connections with Tygon tubing may be used. The manifold distributing the test atmospheres must be sampled simultaneously by the KI sampling train and the instrument to be calibrated. Check assembled systems for leaks. Record the instrument response in nanoamperes at each concentration (usually six). Establish these concentrations by analysis, using the neutral buffered potassium iodide method as follows:

8.2.2.1 *Blank.* With ozone lamp off, flush the system for several minutes to remove residual ozone. Pipet 10 ml. absorbing reagent into each absorber. Draw air from the ozone-generating system through the sampling train at 0.2 to 1 liter/minute for 10 minutes. Immediately transfer the exposed solution to a clean 1-cm. cell. Determine the absorbance at 352 nm. against unexposed absorbing reagent as the reference. If the system blank gives an absorbance, continue flushing the ozone generation system until no absorbance is obtained.

8.2.2.2 *Test Atmospheres.* With the ozone lamp operating, equilibrate the system for about 10 minutes. Pipet 10 ml. of absorbing reagent into each absorber and collect samples for 10 minutes in the concentration range desired for calibration. Immediately transfer the solutions from the two absorbers to clean 1-cm. cells. Determine the absorbance of each at 352 nm. against unexposed absorbing reagent as the reference. Add the absorbances of the two solutions to obtain total absorbance. Read total $\mu g.O_3$ from the calibration curve (see 8.1). Calculate total volume of air sampled corrected to reference conditions of 25° C. and 760 mm. Hg. as follows:

$$V_s = V \times \frac{P}{760} \times \frac{298}{t+273} \times 10^{-3}$$

V_s = Volume of air at reference conditions, $m.^3$

V = Volume of air at sampling conditions, liters.

P = Barometric pressure at sampling conditions, mm. Hg.

t = Temperature at sampling conditions, °C.

10^{-3} = Conversion of liters to $m.^3$

Calculate ozone concentration in p.p.m. as follows:

$$\text{p.p.m. } O_3 = \frac{\mu g.\ O_3}{V_s} \times 5.10 \times 10^{-4}$$

8.2.3 *Instrument Calibration Curve.* Instrument response from the photomultiplier tube is ordinarily in current or voltage. Plot the current, or voltage if appropriate, (y-axis) for the test atmospheres against ozone concentration as determined by the neutral buffered potassium iodide method, in p.p.m. (x-axis).

9. *Calculations.*

9.1 If a recorder is used which has been properly zeroed and spanned, ozone concentrations can be read directly.

9.2 If the DC amplifier is read directly, the reading must be converted to ozone concentrations using the instrument calibration curve (8.2.3).

9.3 Conversion between p.p.m. and $\mu g./m.^3$ values for ozone can be made as follows:

$$\text{p.p.m. } O_3 = \frac{\mu g.\ O_3}{m.^3} \times 5.10 \times 10^{-4}$$

10. *Bibliography.*

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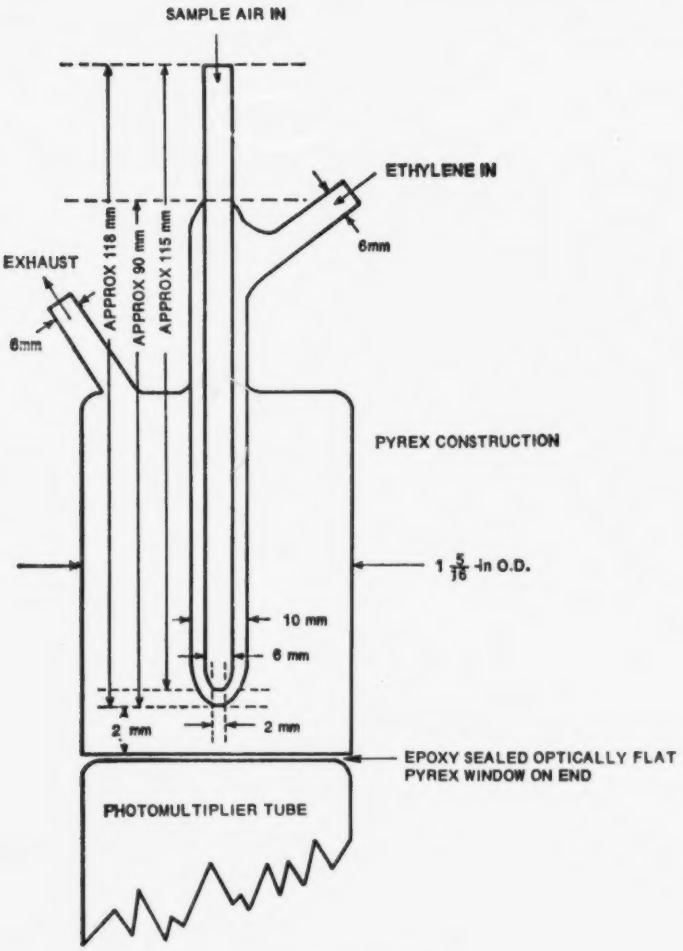

Figure D1. Detector cell.

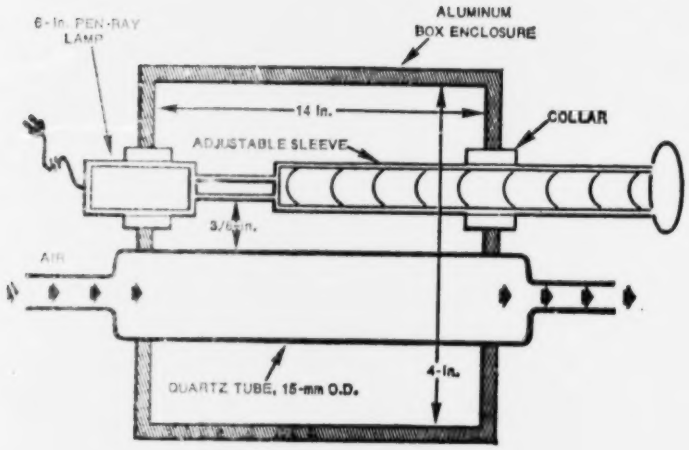

Figure D2. Ozone source.

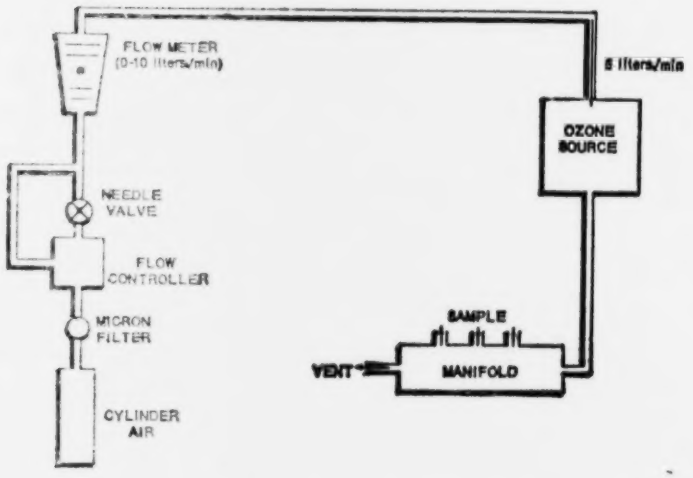

Figure D3. Ozone calibration air supply, source, and manifold system.

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15. Supplementary Notes

16. Abstracts

Guidelines for the quality control of the Federal reference method for photochemical oxidants are presented. These include:

1. Good operating practices
2. Directions on how to assess data and qualify data
3. Directions on how to identify trouble and improve data quality
4. Directions to permit design of auditing activities
5. Procedures for selecting action options and relating them to costs

This document is not a research report. It is for use by operating personnel.

17. Key Words and Document Analysis. 17a. Descriptors

Quality Assurance
Quality Control
Air Pollution
Quantitative Analysis
Gas Analysis
Ozone

17b. Identifiers/Open-Ended Terms

17c. COSATI Field/Group 13H, 14D, 13B, 07D, 14B, 07B

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